California Environmental Protection Agency

Air Resources Board

SOP MLD 059

STANDARD OPERATING PROCEDURE FOR THE DETERMINATION OF OXYGENATED HYDRO-CARBONS (OHCs) IN AMBIENT AIR BY CAPILLARY COLUMN GAS CHROMATOGRAPHY/MASS SPECTROMETRY

Northern Laboratory Branch
Monitoring and Laboratory Division

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1.0 SCOPE

This document describes the procedures followed by Monitoring and Laboratory Division (MLD) staff to analyze oxygenated hydrocarbons by Gas Chromatography with Mass Spectrometry detection, (GC/MS), in ambient air samples collected from the California Toxic Monitoring Network. Staff of the Northern Laboratory Branch (NLB), Organic Laboratory Section (OLS), developed the method. This Standard Operating Procedure (SOP) is based on the following U.S. Environmental Protection Agency (EPA) method:

> Toxic Organic Compounds in Ambient Air Compendium Method TO-15, "Determination of Volatile Organic Compounds (VOCs) In Air Collected In Specially-Prepared Canisters And Analyzed by Gas Chromatography/Mass Spectrometry (GC/MS)", EPA/625/R-96/010b, January 1999.

This SOP, and its predecessor, MLD050,"Standard Operating Procedure for the Determination of Ambient Air Oxygenated Hydrocarbons (OHCs) Using Summa Canisters and Gas Chromatographic Analysis," can be used for several oxygenated hydrocarbons. Table 1, page 27, shows a list of compounds that can be detected by this method. The only compound with data being reported using this SOP is methyl *tert*-butyl ether.

2.0 SUMMARY OF METHOD

Ambient air is collected in a SUMMA polished stainless steel canister using a Xontech 910A sampler. The sampling procedure for Toxic samples is detailed in the Air Resources Board Quality Assurance Manual, Volume II, Appendix Q. All the operational procedures and sampling conditions for each sample are documented in the field. A record of this information is sent back to the OLS along with the sample. Upon receipt, the sample canister pressure is measured with a calibrated external pressure gauge. This information and particulars of the collection are documented in the laboratory. The sample is then analyzed according to the SOP in the laboratory.

An ambient air sample is introduced into the analytical system from a pressurized canister through stainless steel or Teflon tubing with the aid of a mass flow con-

troller (MFC) and a vacuum system. A digital readout attached to the MFC provides a visual indication of the proper sample flow during sampling. Automated sampling of up to 16 canisters can be accomplished using the system's multi-position stream selector valve.

The desired components of the sample are trapped on an adsorbent trap at 10 degrees centigrade (ºC), while fixed gases, such as nitrogen (N_2), oxygen (O_2), carbon dioxide (CO_2) pass through the adsorbent trap to the vent. Following the sample stream, the adsorbent trap is purged with dry, ultrapure N_2 to flush sample remaining in the tubing or valving onto the adsorbent trap. This step also allows additional minimally adsorbed non-target compounds, like methane (CH_4) and especially water, to pass through the adsorbent trap to vent. After purging, the adsorbent trap is rapidly heated to 200 ºC to desorb and reconcentrate the contents onto a cryofocuser at -130^{o}C. The cryofocuser is rapidly heated to 200^{o}C to desorb the trapped components onto a DB-VRX capillary column.

The trapped sample mixture is separated into individual components by their interaction with the capillary column's stationary phase, using temperature-programmed gas chromatography. A Mass Selective Detector (MSD) detects the components eluting from the column. The analytes are subsequently identified and quantified. Identification of a component in a sample is based upon both the retention time and mass spectral matching. The response of one mass fragment, the Primary Quantitation Ion, is used for quantitation.

3.0 INTERFERENCES AND LIMITATIONS

3.1 Although studies have shown that the target compounds can be considered stable in stainless steel canisters, every effort must be made to analyze the sample as soon as possible. Extreme care must be taken to prevent contamination during sample collection, transportation and subsequent analysis.

3.2 The MSD should be setup and tuned according to the manufacturer's specifications prior to sample analysis.

3.3 Although the retention time of an analyte is not the only parameter used in identifying a component in GC/MS, the retention times of the GC portion of the system must be reproducible.

3.4 All target compounds are identified by their mass spectrum and retention times. Compounds having similar GC retention times may co-elute. This can lead to misidentification or inaccurate quantitation. The use of a Primary Quantitation Ion, as well as secondary ions, may allow accurate quantitation and identification even under these circumstances. There is no substitute, however, for good chromatographic separation.

3.5 Very low target and non-target analyte concentrations may not produce a good quality spectrum. This may result in either low match quality or misidentification.

3.6 No more than 10 samples should be run consecutively without system recalibration. This is an internal OLS/SOP specific requirement, not a Laboratory Quality Control Manual requirement.

3.7 The analytical system may be contaminated when samples containing high compound concentrations are analyzed. A blank should be analyzed after a high concentration sample to check for possible carryover.

3.8 High boiling compounds being trapped on the column may cause daily baseline shifting, or the appearance of broad, extraneous "ghost" peaks. The column should be baked out prior to each set of analytical runs to remove these contaminants. The bake out temperature should not exceed the column's maximum operating temperature of 260 ºC.

Reference: "1996/1997 Catalog and Technical Reference", J & W Scientific, Inc.

3.9 The analytical system is capable of detecting compounds other than MTBE. Table 1, page 27, lists the compounds detected by this procedure.

4.0 APPARATUS

4.1 A Lotus Consulting/Varian Model 3800 gas chromatograph, consisting of:

4.1.1 Electronic Flow Controller(s) (EFC) for automatic control of the chromatographic column He carrier flow(s). One or more of this type EFC may be installed, but only one is required for this procedure.

4.1.2 Electronic Flow Controller(s) (EFC) for automatic control of Flame Ionization Detector gas flow (Hydrogen, Air, and N_2). One or more of this type EFC may be installed, but none are required for this procedure.

4.1.3 Seven temperature programmable zones to accommodate injectors, detectors, valves, and additional devices as needed.

4.1.4 A chromatographic column oven with programmed temperature control.

4.1.5 Seven time programmable relays for control of valves or other timed events.

4.1.6 A keypad for entering setpoints for items 4.1.1 through 4.1.5 above, independent from the attached Workstation.

4.1.7 Manual, digital flow controllers, and Manual pressure regulators for setting He and N_2 purge/sweep flows and/or pressures. The digital flow controllers are calibrated to deliver gas flows from zero to 100 cm^3/min, $\pm$ 3%, with an inlet pressure of 80 psi.

4.1.8 Three analog pressure gauges for use in gas monitoring and diagnosing problems with the flow system.

4.1.9 An Cryogenic/Adsorbent Concentration system, containing:

4.1.9.1 An electrically actuated multi-position Stream Selector Valve (SSV).

4.1.9.2 Tubing to connect canisters to the SSV.

4.1.9.2.1 Examples of tubing size and material are $^1/_8$-inch teflon tubing, $^1/_{16}$ inch stainless steel tubing, $^1/_{16}$ inch nickel tubing, or $^1/_{16}$ inch glass lined stainless steel tubing.

4.1.9.2.2 Canisters may be connected by tubing to a manifold and then the manifold connected to the automated sampler's SSV.

4.1.9.2.3 Canisters can also be connected by tubing directly to the sampler's SSV.

4.1.9.2.4 Tubing connected to the SSV either from the manifold or directly from the canisters is heated.

4.1.9.2.5 Tubing connecting canisters to a manifold may or may not be heated.

4.1.9.3 A low-pressure regulator (LPR) with a teflon lined diaphragm.

4.1.9.4 A Mass Flow Controller (MFC) with a Control/Digital Readout module.

4.1.9.4.1 The MFC is mounted downstream of the SSV and other sampling components, to eliminate contamination and to reduce the volume of the sampling lines.

4.1.9.4.2 The MFC is typically rated at 100 cm3 /min at 100% full scale. The flow rate is set as a percentage of full scale. For example, a flow rate of 50 cm^3/min corresponds to a setting of 50% full scale.

4.1.9.4.3 The Control/Digital Readout module is set to the side or on top of the GC.

4.1.9.4.4 A rotometer and analog vacuum gauge are mounted on the GC, between the MFC and the vacuum source, to allow visual confirmation of flow and vacuum pressure.

4.1.9.5 A fixed volume Sample Loop for addition of an internal standard, if required.

4.1.9.6 Five to eight electrically activated valves, as required.

1.1.1.7 A 700 µl, 1/8-inch adsorbent trap, constructed of nickel tubing and packed with 60/80 Carbopack B, Carbopack C, and Carboxen 1000.

4.1.9.8 A 100 µl, 1/16 inch cryofocuser constructed of 0.04 inch internal diameter (i.d.) nickel tubing, without packing.

4.1.9.9 Reference: "Stream Selector Valve Control Software For Varian Star Workstation Operator's Manual", by Randall Bramston-Cook of Lotus Consulting.

4.1.10 A Varian Saturn Model 2000 Ion Trap Detector (ITD) interfaced to the Lotus/Varian Saturn 3800 GC.

4.1.10.1 This detector is of ion trap design and is capable of scanning from 10 to 650 atomic mass units (amu).

4.1.10.2 The detector is operated in the electron impact mode at 70 electron volts (eV).

4.1.11 Information and instruction on the proper operation of the Varian Model 3800 Gas Chromatograph and the Varian Saturn Model 2000 Ion Trap Detector can be found in the associated manuals.

4.2 A functionally equivalent system to that of Section 4.1, consisting of:

4.2.1 A Lotus Consulting/Varian Model 3800 gas chromatograph configured as a stand-alone Adsorbent/Cryogenic Concentration System. It

is as described in Section 4.1 above, less the ITD of Section 4.1.10,

4.2.2 An Agilent Model 6890 gas chromatograph, consisting of:

4.2.2.1 Electronic Pneumatic Controller(s) (EPC) for control of carrier gas, make-up gas, and detector gases. One or more of this type EPC may be installed, but none are required for this procedure.

4.2.2.1.1 The Agilent carrier gas EPC is not used in this procedure. Carrier gas control is performed by the Lotus Consulting/Varian Model 3800 gas chromatograph (Section 4.1.1 above).

4.2.2.1.2 The Agilent detector gas EPC is not used in this procedure. They can be used to control optional GC detectors.

4.2.2.2 A chromatographic column oven with programmed temperature control.

4.2.2.3 An Agilent Model 5973 Mass Selective Detector (MSD) interfaced to the HP 6890 GC.

4.2.2.3.1 The detector is a quadrupole mass spectrometer, capable of scanning from 2 to 800 amu.

4.2.2.3.2 The detector is operated in the electron impact mode at 70 eV.

4.2.3 Information and instruction on the proper operation of the Varian Model 3800 Gas Chromatograph, the Agilent Model 6890 Gas Chromatograph, and the Agilent Model 5973 Mass Selective Detector can be found in the associated manuals.

4.3 A J&W DB-VRX 60 m by 0.25-mm i.d., with 1.40 μm film thickness, fused silica capillary column.

Reference: "1996/1997 Catalog and Technical Reference", J & W Scientific, Inc.

4.4 A Varian Saturn GC/MS or GC Workstation that includes an Intel compatible PC, an Ethernet network adapter, Microsoft 9.X, NT 4.0, or newer, operating system, and Varian Saturn or Star Chromatography Workstation software.

4.4.1 The GC/MS Workstation is used for GC configuration, ITD configuration, sample file lists, sequence lists, method building, storage of raw

data files and the subsequent processing of the raw data to produce qualitative/quantitative data. It is used with the system described in Section 4.1 above.

4.4.2 The GC Workstation is used for GC system configuration, sample file lists, sequence lists, and method building. This Workstation is used in the equivalent system described in Section 4.2 above.

4.4.3 The Ethernet network adapter card provides digital communication with the GC.

4.4.4 The GPIB interface card provides digital data communication with the ITD.

4.4.5 Reference: Manuals, on CD-ROM, “Varian Star Chromatography Workstation”, Version 5.5, by Varian, Inc. (P/N 03-910818-01.4)

Manuals, on CD-ROM, “Varian Saturn GC/MS Workstation – System Software”, Version 5.52, by Varian, Inc. (P/N 03-910876-01)

"Varian GC Star Workstation Manual", by Randall Bramston-Cook of Lotus Consulting

4.5 An Agilent GC/MS ChemStation that includes an Intel compatible PC, an Ethernet network adapter, a GPIB interface card, Microsoft 9.X, NT 4.0, or newer, operating system, and Agilent Analytical MSD Productivity ChemStation Software.

4.5.1 This ChemStation is used in the equivalent system described in Section 4.2 above.

4.5.2 The ChemStation is used for storage of raw data files and the subsequent processing of the raw data to produce qualitative/quantitative data.

4.5.3 The Ethernet network adapter card provides digital communication with the GC.

4.5.4 The GPIB interface card provides digital data communication with the MSD.

4.5.5 Reference: Manuals, on CD-ROM, “HP 5973 MSD Reference Collection”, Revision C.00.00, by Agilent

4.6 The Star Chromatography Workstation and the Agilent Analytical MSD Productivity ChemStation software can be operated from the same Intel compatible PC.

4.7 Stainless steel SUMMA passivated canisters for sample collection and standard preparation.

5.0 REAGENTS

5.1 A system blank/canister blank, consisting of zero air, ultrapure air, Grade 5 N_2, or ultrapure N_2, in a SUMMA canister that has been humidified with 150 µl of HPLC grade water. Alternatively, Ultrapure or Grade 5 N_2, sampled directly from a gas cylinder, or headspace N_2, sampled directly from a Liquid Nitrogen (LN_2) dewar can be substituted as the system blank.

5.2 A certified National Institute of Standards (NIST) standard calibration mixture, or mixtures, containing all analytes of interest. This standard, or standards, should be slightly higher in concentration than the typical sample and must be within the dynamic range of the GC/MS system. Table 2, page 28, lists the NIST Standards associated with this SOP. Appendix I, page 57, lists the concentrations of the NIST standard, or standards, associated with this SOP.

5.3 A control standard mixture, or mixtures, containing all analytes of interest at concentrations within the calibration range of the GC System. Table 2, page 28, lists the Control standard, or standards, associated with this SOP. Appendix I, page 57, lists the concentrations of the Control standard, or standards, associated with this SOP.

5.4 One high pressure gas cylinder of Grade 5 or better Helium (He) for use as the GC column carrier gas and in cryogenic/adsorbent trap and cryofocuser purging.

5.5 One high pressure gas cylinder of Grade 5 or better Nitrogen (N_2) for use in sample line purging, sample loop purging, cryogenic/adsorbent trap dry purging, and leak testing.

5.6 One LN_2 dewar for cooling the cryogenic/adsorbent trap, the cryofocuser, and the GC column oven. This N_2 can be used as the system blank.

5.7 Perfluorotributylamine (FC43) for use in MS tuning.

5.8 A 2 part per million (ppm) solution of 1-bromo-4-fluorobenzene (BFB) for MS tuning verification. This optional procedure **is not** a requirement of this SOP.

6.0 INSTRUMENT CONFIGURATION AND PARAMETERS

6.1 A Lotus Consulting/Varian Model 3800 Gas Chromatograph, with a Cryogenic/Adsorbent Concentration System, handles concentration of the sample and introduction of the concentrated sample onto the gas chromatographic column (see Section 4.1 above). It controls the temperature of the valve ovens and injectors (Section 4.1.3 above), the GC column oven (4.1.4 above), the carrier gas flow (4.1.1 above), and the relay time programs (4.1.5 above). The Varian Saturn Model 2000 Ion Trap Detector (ITD) interfaced to the Lotus/Varian Saturn 3800 GC (4.1.10 above) has independent control of it's electronics and heated zones. A listing of the Varian Saturn Workstation methods, which includes the GC and ITD setpoints controlled by the Workstation, is given in Appendix II, page 59.

6.1.1 The gas flow and automation configurations, the location and name of the heated zones, and location of the valves associated with the 3800 GC are shown in Figure 1, page 42, through Figure 7, page 49. The nomenclature and function of the GC thermal zones are shown in Table 3, page 29. Each major item from the 3800 GC Section in the acquisition method is described.

6.1.1.1 Front Valve Oven / Front Small Valve Oven (Heated Zone 5)

This setting controls the temperature of the heated valve oven in which Valve 3 (V3) and Valve 4 (V4) are installed (page 64).

6.1.1.2 Middle Valve Oven / Large Valve Oven (Heated Zone 4)

This setting controls the isothermal temperature of the sample lines extending from the Sampling Manifold to the SSV (page 64).

6.1.1.3 Rear Valve Oven / Large Valve Oven (Heated Zone 3)

This setting controls the temperature of the heated valve oven in which the SSV (Section 4.1.9.1 above), Valve 1 (V1), and Valve 2 (V2) are installed (page 64).

6.1.1.4 Valve Table

These settings control the action of the seven time programmable valves/events of the Varian 3800 GC (page 64). The valve/relay number, the valve/relay name, the relay

state, and the function at each state, are given in Table 4, page 31.

6.1.1.5 Front Injector Type 1079 (heated Zone 1)

This setting controls the temperature of the Cryogenic/-Adsorbent Trap (page 65).

6.1.1.6 Middle Injector Type 1079 (Heated Zone 2)

This setting controls the temperature of the Cryofocuser/ (page 66).

6.1.1.7 Rear Injector EFC Type 3

This setting controls the He capillary column flow rate (page 66).

6.1.1.8 Column Oven

This setting controls the temperature of the GC Column oven (page 66).

6.1.2 Each major item from the MS METHOD SECTION REPORT Section in the acquisition method is described below.

6.1.2.1 Security Options Required, Mass Data Type, and Number of Segments

The Security Options Required and Mass Data Type are set to EI (Electron Impact) and CENTROID, as opposed to PROFILE, for this procedure. The number of segments refers to the time programmable scanning regions used by the method, discusses in 6.1.2.4 below.

6.1.2.2 Method Start Time

The Method Start Time is defined as “The time to flush the system before sample collection begins plus the actual sampling time.” In essence, this allows the system start time to begin at 0, by allowing the valve table functions (see the Valve Table in the acquiring method) to occur in “negative” time. It is set equal to the time required to trap, cryofocus, and begin desorption onto the GC column.

6.1.2.3 Flow Sampling Segment

When connected to the MFC, the software can control the MFC setpoint (see Section 4.1.9.4.2 above). The Start Time and End Time (in "negative" time) can be referenced on the report. This Segment is **not** active in this procedure.

6.1.2.4 Segment Number [X]

Each Segment Section contains the ITD/MS parameters that govern data acquisition by the detector. Each Segment encompasses a different time period from the run. If the Segment is set for acquisition, the scan segments that make up the total amu scan range are also shown in this Section.

6.1.3 The MS REPORT FORMAT METHOD Section in the quantitation method defines how reports and Reconstructed Ion Chromatogram (RIC) will be printed.

6.1.4 The DATA HANDLING METHOD Section in the quantitation method defines both the general calculation setup and the compound specific data, as shown in the MTBE portion of the quantitation method. This data is updated during the data processing cycle.

6.1.5 The Trap Temperature, Manifold Temperature, and Transfer Line Temperature are set from within the Instrument Control section of the software (see page 85). They are not recorded/reported with the method, but are recorded in each sample run file and reported in each individual sample report.

6.2 In the functionally equivalent system, a Lotus Consulting/Varian Model 3800 gas chromatograph is configured as a stand-alone Adsorbent/Cryogenic Concentration System. It handles concentration of the sample and introduction of the concentrated sample onto the gas chromatographic column (see Section 4.2.1 above) and controls the temperature of the valve ovens and injectors, the carrier gas flow, and the relay time programs. An Agilent Model 6890 gas chromatograph controls the GC column oven. An Agilent Model 5973 Mass Selective Detector (MSD), interfaced to the Agilent GC, has independent control of its electronics and heated zones. A listing of the Varian Star Workstation methods, which includes the GC setpoints controlled by the Workstation, is given in Appendix III, page 89. A listing of the Agilent GC/MS Chemstation method, which includes all of the GC and MSD setpoints controlled by the Chemstation, is given in Appendix IV, page 95.

6.2.1 The gas flow and automation configurations, the location and name of the heated zones, and location of the valves associated with the 3800

GC are essentially identical to those shown in Figure 1, page 42, through Figure 7, page 49. Rather than and Ion Trap Detector, the column effluent is transferred to a Mass Selective Detector. The nomenclature and function of the GC thermal zones are shown in Table 5, page 33. Each major item from the 3800 GC Section in the acquisition method is described.

6.2.1.1 Middle Valve Oven / Middle Small Valve Oven (Heated Zone 5)

This setting controls the temperature of the heated valve oven in which the SSV (Section 4.1.9.1 above), Valve 1 (V1), and Valve 2 (V2) are installed (page 90).

6.2.1.2 Rear Valve Oven / Rear Large Valve Oven (Heated Zone 3)

This setting controls the isothermal temperature of the sample lines extending from the Sampling Manifold to the SSV (page 90).

6.2.1.3 Valve Table

These settings control the action of the seven time programmable valves/events of the Varian 3800 GC (page 90). The valve/relay number, the valve/relay name, the relay state, and the function at each state, are essentially identical to those shown in Table 4, page 31. Valve/relay 5 is not used for the Internal Standard. The internal standard valve, if activated, is synchronized with Valve 1.

6.2.1.4 Front Injector Type 1079 (heated Zone 1)

This setting controls the temperature of the Cryogenic/-Adsorbent Trap (page 91).

6.2.1.5 Middle Injector Type 1079 (Heated Zone 2)

This setting controls the temperature of the Cryofocuser/ (page 91).

6.2.1.6 Rear Injector Type 1041 (Heated Zone 6)

This setting controls the temperature of the heated valve oven in which Valve 3 (V3) and Valve 4 (V4) are installed (page 92).

6.2.1.7 Rear Injector EFC Type 3

This setting controls the He capillary column flow rate (page 92).

6.2.2 Each major item from the HP6890 GC Section in the acquisition method is described below.

6.2.2.1 Oven

This setting controls the temperature of the GC Column oven (page 96).

6.2.2.2 Thermal Auxiliary Zone 2

This setting controls the temperature of the transfer line between the GC and the MSD (page 97).

6.2.3 Each major item from the MS ACQUISITION Section in the acquisition method is described below.

6.2.3.1 General Information

This Section shows the MSD tune file used and the type of acquisition.

6.2.3.2 MS Information

This Section has settings to control the solvent delay and the final electron multiplier voltage. The former is the time to wait, after the GC/MSD start, until turning on the ionization filament. The latter is the final Electron Multiplier voltage after any Offset.

6.2.3.3 Scan Parameters

This section contains setpoints for the mass range to scan, the response threshold, and the sampling/AD frequency.

6.2.3.4 MS Zones

This section contains setpoints for the quadrupole oven temperature and the ionization source temperature.

6.2.4 Each major item from the DATA ANALYSIS Section in the acquisition method is described below.

6.2.4.1 Data Analysis Parameters

These values define the general calculation setup including reporting and qualitative/quantitative options for the processing of acquired data.

6.2.4.2 Compound Information

These values show the compound specific data, as shown in the MTBE portion of the quantitation method. This data is updated during the data processing cycle.

6.3 The sample volume for the column injection is automated by the Varian Saturn GC/MS or GC Workstation software and the MFC (Section 4.1.9.4). The nominal setpoint for the MFC is shown in Appendix V, page 103.

7.0 DAILY OPERATION

7.1 Instrument Performance Check

7.1.1 The Lotus Consulting/Varian Model 3800GC/Saturn ITD System (Section 4.1 above).

7.1.1.1 Periodic and Daily Tuning

7.1.1.1.1 A complete ITD/MS Autotune is performed approximately every **two weeks**. It includes the Air/Water check, the Electron Multiplier tune, and the Mass Calibration tune. Table 6 shows results of a typical Autotune run.

7.1.1.1.2 The Air/Water check is performed **daily**.

7.1.1.1.3 The Mass Calibration tune with FC43, to meet the tuning and standard mass spectral abundance criteria, is performed **daily** prior to initiating any data collection.

7.1.1.1.4 The procedure and tuning criteria for he Saturn ITD can be found in the Varian system manuals referenced in Appendix III, page 89.

7.1.1.2 The Air/Water check is evaluated **daily**, prior to data collection.

7.1.1.3 The Mass Calibration tune values, with regard to positions and abundance ratios of the m/z's and their corresponding

isotope m/z's, are reviewed **daily**, prior to data collection.

7.1.2 The functionally equivalent system, consisting of a Lotus Consulting/-Varian Model 3800 gas chromatograph configured as a stand-alone Adsorbent/Cryogenic Concentration System, an Agilent Model 6890 gas chromatograph with an Agilent Model 5973 MSD (Section 4.2 above).

7.1.2.1 Periodic and Daily Tuning

7.1.2.1.1 The MSD Autotune is performed **daily**. Table 7 shows results of a typical Autotune run.

7.1.2.1.2 The Mass Calibration tune with FC43, to meet the tuning and standard mass spectral abundance criteria, is performed **daily** prior to initiating any data collection.

7.1.2.1.3 The tuning procedure and criteria for the Agilent MSD can be found in the Agilent system manuals referenced in Appendix IV, page 95.

7.1.2.2 The Mass Calibration tune values, with regard to positions and abundance ratios of the m/z's and their corresponding isotope m/z's, are reviewed **daily**, prior to data collection.

7.2 Initial Setup

7.2.1 The Lotus Consulting/Varian Model 3800GC/Saturn ITD System (Section 4.1 above).

7.2.1.1 The Varian 3800 GC/ITD method (.mth), sample list (.smp), and sequence list (.seq) are set up on the Saturn GC/MS Workstation.

7.2.1.2 The MTBE.MTH, page 60, shows a listing of the acquiring method. Screen shots of the sample list and sequence list and shown on pages 86 and 87.

7.2.2 The functionally equivalent system, consisting of a Lotus Consulting/-Varian Model 3800 gas chromatograph configured as a stand-alone Adsorbent/Cryogenic Concentration System, an Agilent Model 6890 gas chromatograph with an Agilent Model 5973 MSD (Section 4.2 above).

7.2.2.1 The Varian 3800 GC method (.mth), sample list (.smp), and

sequence list (.seq) are set up on the Star GC Workstation. A listing of the acquiring method, MLD050B.MTH is shown on page 90. Screen shots of the sample list and sequence list and shown on pages 86 and 87.

7.2.2.2 The Agilent 6890/5973 GC/MSD method (.m), sample list (.smp), and sequence list (.seq) are set up on the HP Chemstation. A listing of the acquiring method, MLD050M.M, is shown on page 96. A screen shot of the sequence list is shown on page 102.

7.2.3 The sample flow rate setting is confirmed on the MFC's Control/-Digital Readout module. The sample volume is determined as the product of the trapping time, in minutes, times the flow rate, in cm^3/-min, set on the MFC. Confirmation of the actual flow rate can be done with an external flow meter. For example:

Trapping Time:	3.0 minutes
Flow Rate:	50.0 cm3/min
Volume:	3.00 min x 50.0 cm3/min = 150 cm3

7.2.4 Canister samples are connected to the canister sampling manifold using appropriate tubing and fittings (Section 4.1.9.2 above). The sample canister valves are opened and the canister pressure gauge is monitored to assure a leak-free connection. The initial canister pressure is recorded.

7.3 Sample Concentration and Analysis

7.3.1 Samples are introduced into either system's Cryogenic/Adsorbent Concentrator (Section 4.1.9) under control of the 3800 GCs Valve Table, described in Section 6.1.1.4 or 6.2.1.3.

7.3.1.1 The gas and sample flows during the cryo/adsorbent loading steps are shown in Figure 1, page 42, through Figure 4, page 46.

7.3.1.2 The gas and sample flows during the cryofocuser loading and isolation steps are shown in Figure 5, page 47, through Figure 6, page 48.

7.3.1.3 The cryofocuser is heated to desorb the sample onto the GC column, as shown in Figure 7, page 49.

7.3.1.4 The program times, relay # and status, and a description of the events are shown in Table 8, page 37.

7.3.1.5 A graphical representation of the concentration steps is given on page 50.

7.4 Samples

7.4.1 A system blank (defined in Section 5.1, page 8) is analyzed prior to calibration standards, controls and samples.

7.4.1.1 A system blank run must be performed at the beginning of every run at least once every 24 hours.

7.4.1.2 System blanks must also be run after samples, which are known or suspected to contain high concentrations of target analytes, to detect and eliminate possible carry-over. For example, high standards or samples with >100 times a target compound's LOD.

7.4.1.3 Trip blanks, if available, are analyzed like samples and their results are documented and evaluated.

7.4.2 A daily calibration standard, for each standard mixture in use (defined in Section 5.2, page 8), is analyzed after the system blank, prior to controls or samples.

7.4.3 A control standard, for each control mixture in use (defined in Section 5.3, page 8), is analyzed after the system blank and calibration standards, prior to samples.

7.4.4 Ambient samples are analyzed using the same sample volume as used for the calibration standard and control standard.

7.4.4.1 A smaller volume is analyzed for samples containing concentrations of target analytes that exceed the calibrated range of the analysis.

7.4.4.2 Smaller volumes are obtained by reducing the trapping time while keeping the MFC setpoint constant.

7.4.5 Duplicate analyses are performed on 10% of all ambient samples analyzed.

7.5 A summary of the Daily Procedures for running the Varian Saturn System and the Varian/Agilent System are given in Appendix VI and Appendix VII respectively.

8.0 DATA ANALYSIS

8.1 After data acquisition, the raw data files collected on either the Varian Saturn GC/MS Workstation or the Agilent GC/MS Chemstation are processed by the software. The result files contain the integrated Primary Quantitation Ion peak areas, retention times, and mass spectra.

8.2 Chromatographic peaks found in the Total Ion Chromatogram (TIC) in the result files for calibration standards are qualitatively identified based on matching the mass spectrum to a reference spectra and the retention time to the reference retention time. Both of these references are stored in the method.

8.3 After analyte identification, the integrated calibration standard areas for the Primary Quantitation Ions are used to calibrate the Workstation method for both retention time and concentration. The latter is based on the peak areas and the known analyte concentration in the standards.

8.4 After calibration of the method, chromatographic peaks from the TIC in blank, control, and ambient sample result files are qualitatively identified based on matching the mass spectrum to a reference spectra and the retention time to the reference retention time. They are quantified using the Primary Quantitation Ion response factor stored in the method.

8.5 A typical Calibration Standard TIC, Ambient Air TIC, and Mass Spectrum are shown in Figure 9, Figure 10, and Figure 11 (pages 51, 52 and 53).

9.0 QUALITY CONTROL

9.1 System Blank

9.1.1 A system blank is analyzed before any standard or sample is run to evaluate the system cleanliness.

9.1.1.1 If the individual concentrations of any target analytes detected in the system blank are less than two times their LOD, no action is taken.

9.1.1.2 If the concentration of any target analyte detected in the system blank is greater than five times its LOD, the analytical run associated with the system blank should be invalidated and the cause investigated.

9.1.1.3 If the individual concentrations of any target analytes detected in the system blank are greater than two, but less than five times their LOD, each individual analyte result in

the blank should be compared to each individual analyte result for each sample analyzed.

9.1.1.3.1 If the analyte result in the blank is less than five percent (5%) of the analyte result in the sample, no action should be taken.

9.1.1.3.2 If the analyte result in the blank is greater than five percent (5%) of the analyte result in the sample, the sample result should be invalidated.

9.1.2 All actions taken in response to system blank results should be approved by the OLS Supervisor.

9.1.3 The actions taken in response to system blank results are may be modified by the most current version of the Laboratory Quality Control Manual in effect.

9.2 Daily Calibration

9.2.1 A single point calibration is performed daily by analyzing the calibration standard, or standards.

9.2.2 Retention times, spectra and the Primary Quantitation Ion integration for each target analyte in the calibration standard run should be thoroughly checked prior to calibration.

9.2.2.1 The retention times should fall within ± 0.1 minute of the preceding runs retention times. This difference may be modified if historical data indicates a larger difference is more appropriate (i.e., volatile early eluting compounds, or wider, later eluting compounds).

9.2.2.2 The Primary Quantitation ion response factors should fall within ± 20% of the preceding runs response factors.

9.2.2.3 If either retention times or the response factors are outside these ranges, the analyst must investigate the cause.

9.2.3 The Workstation method is updated after every run with the new calibration information.

9.2.4 The method and response factors can be printed for a hardcopy record.

9.3 Control Standard

9.3.1 In order to evaluate the accuracy of the calibration and the overall performance of the system, a control standard is analyzed daily following the system blank and the calibration standard and prior to sample analysis.

9.3.2 Analysis results of the target analytes in this standard are recorded and used to generate control charts.

9.3.2.1 At least 20 data points are needed for the initial set of control limits, and any subsequent adjustment of these limits. This is a requirement for this SOP.

9.3.2.2 A Typical Control Chart for MTBE is shown in Figure 12, page 54.

9.3.2.3 A typical dataset used for calculating control limits is given in Table 9, page 41.

9.3.3 The control standard results must be within the established Control Limits for sample analyses to be valid. Control standard results are evaluated as follows.

9.3.3.1 Should any analysis of the control standard yield a result that falls outside the established Control Limits, the control standard shall be reanalyzed.

9.3.3.2 If the second result is also outside the Control Limits, the analysis shall be discontinued and the problem investigated.

9.3.3.3 All data generated during the out of control period shall be invalidated, and the samples reanalyzed after the analysis has been reestablished.

9.3.3.4 If reanalysis is not possible, results may be invalidated on a compound by compound basis.

9.3.4 All actions taken in response to system blank results should be approved by the OLS Supervisor.

9.3.5 The actions taken in response to control standard results may be modified by the most current version of the Laboratory Quality Control Manual in effect.

9.4 Method Precision

9.4.1 Sample precision is measured by the analysis of ambient duplicate samples and the analysis of ambient collocated samples.

9.4.2 The percent difference (PD) of the duplicate analyses, for samples with target analyte concentrations greater than five (5) times the Limit of Detection (LOD), are recorded and included in the method quality control report.

9.4.2.1 The control limits for the PD of the duplicate sample analyses are the same as the control limits for the Control Standard.

9.4.2.2 For this analysis, if the duplicate results do not meet the quality control criteria, the samples associated with the duplicate pair should be reanalyzed, or invalidated if reanalysis is not possible.

9.4.3 The PD for collocated sample analyses is used to evaluate method precision for both sampling and analysis procedures.

9.4.3.1 The PD for collocated sample analyses should be within ± 25%.

9.4.3.2 Collocated sample results that do not meet the criteria are reported to the Air Quality Surveillance Branch for action.

9.4.3.3 Results for collocated samples that do not meet the criteria are not invalidated by the Laboratory.

9.4.4 All actions taken in response to duplicate sample results should be approved by the OLS Supervisor.

9.4.5 The actions taken in response to duplicate sample results may be modified by the most current version of the Laboratory Quality Control Manual in effect.

9.5 Multipoint Analysis Verification

9.5.1 A multipoint verification must be performed every year, as dictated in the most current version of the Laboratory Quality Control Manual, to verify the precision and the calibration working range.

9.5.1.1 A multipoint verification is also required, as dictated in the most current version of the Laboratory Quality Control Manual, whenever a system change occurs that is defined by

the analyst as major (i.e., a change in instrument or measurement technique that would likely change the method LOD, linearity, or measured concentrations).

9.5.1.2 This is done by analyzing at least three (3) concentration levels of the NIST standard, using at least three (3) replicates at each level.

9.5.1.3 One of the multipoint verification points must be at the same concentration level as the daily calibration standard level.

9.5.1.4 One of the points should be near the LOD concentration of the target analytes.

9.5.1.5 The highest concentration point determines the upper limit of the analytical concentration range.

9.5.2 In order to verify that the system is linear:

9.5.2.1 The plot of response vs. concentration must appear linear, and;

9.5.2.2 The correlation coefficient, r, calculated from a least square fit of the response/concentration data must be 0.98 or greater. This corresponds to a coefficient of determination, r^2, of 0.96 or greater.

9.5.3 A typical multipoint data set and graph for MTBE is presented in Figure 13, page 55. The correlation coefficient and highest calibrated concentration values for MTBE is shown Appendix VIII, page 113.

9.5.4 If the verification is considered substantially different from an initial or immediately preceding check, by either the analyst or the OLS Supervisor, the analytical system should be evaluated for problems and the procedure repeated.

9.5.5 All actions taken in response to the multipoint verification should be approved by the OLS Supervisor.

9.5.6 The actions taken in response to the multipoint verification may be modified by the most current version of the Laboratory Quality Control Manual in effect.

9.6 Limit of Detection (LOD) Verification

9.6.1 The LOD verification must be performed every year, as dictated in the most current version of the Laboratory Quality Control Manual,

9.6.1.1 It must also be verified when the conditions listed under multipoint calibration verification, Section 9.5.1 above, occur.

9.6.1.2 This is done by analyzing at least seven (7) replicates of the NIST standard.

9.6.1.3 The concentration must be no more than five times the published LOD.

9.6.1.4 The calculated LODs must be equal to or less than the published LOD values.

9.6.2 The LOD is calculated using the following equation, as specified in most current version of the Laboratory Quality Control Manual in use.

$$\mathbf{MDL} = \mathbf{T}_{(n-1,\,1-\alpha=0.99)} \times \mathbf{s} \qquad \textbf{(1)}$$

where

n = the number of replicates;
T = the Students' t-value at the 99% confidence level (1 - α) for n - 1 degrees of freedom;
s = the Standard Deviation of the sample Mean.

9.6.3 The published LODs for most target analytes analyzed by this method and example verification values are presented in Appendix VIII, page 113.

9.6.4 If the verification is considered substantially different from an initial or immediately preceding check, by either the analyst or the OLS Supervisor, the analytical system should be evaluated for problems and the procedure repeated.

9.6.5 All actions taken in response to the LOD verification should be approved by the OLS Supervisor.

9.6.6 The actions taken in response to the LOD verification may be modified by the most current version of the Laboratory Quality Control Manual in effect.

9.7 Method Accuracy

9.7.1 Providing performance audits to the NLB, in order to assess the accuracy of the generated data, is the responsibility of the Quality Assurance Section (QAS) of the Quality Management Branch (QMB).

9.7.1.1 The analysis of performance audit materials shall follow the same procedures as the analysis of regular samples, where possible.

9.7.1.2 Several replicate analyses of the performance audit material should be performed to provide an estimate of precision (i.e., the sample standard deviation).

9.7.1.3 The concentration results of audit sample analyses, including the sample standard deviation and the number of replicate analyses, shall be provided as quickly as possible to the QAS staff, and shall be included in the quarterly QC reports.

9.7.1.4 If after receiving the QAS Audit Report any results are considered substantially different from the preceding audit results, the OLS Supervisor in conjunction with the QAS Supervisor shall formulate an appropriate course of action.

9.7.1.5 All actions taken in response to the performance audit should be approved by the OLS Supervisor.

9.7.1.6 The actions taken in response to the performance audit may be modified by the most current version of the Laboratory Quality Control Manual in effect.

9.7.2 Providing blind Through the Probe audit samples to the NLB, in order to assess the accuracy of the entire sampling and analysis system, is the responsibility of the Quality Assurance Section (QAS) of the Quality Management Branch (QMB).

9.7.2.1 Through the Probe audit samples shall be treated as regular ambient air samples.

9.7.2.2 Replicate analyses of Through the Probe audit samples, unless the sample is picked as the analytical duplicate, should not be performed.

9.7.2.3 The concentration results of Through the Probe audit sample analysis shall be provided as quickly as possible to the

QAS staff, and shall be included in the quarterly QC reports.

9.7.2.4 If after receiving the QAS Through the Probe Audit Report any results are considered substantially different from the preceding audit results, the OLS Supervisor in conjunction with the QAS Supervisor shall formulate an appropriate course of action.

9.7.2.5 All actions taken in response to Through the Probe audit should be approved by the OLS Supervisor.

9.7.2.6 The actions taken in response to the Through the Probe may be modified by the most current version of the Laboratory Quality Control Manual in effect.

9.7.3 The analysis of any audit samples provided by other sources should be performed as directed by the OLS Supervisor.

9.7.4 Method accuracy may also be assessed by periodically analyzing other standard reference materials (i.e., other NIST Standards). The results of replicate analysis of these materials should be consistent with the estimated uncertainty of the sample, the standard, and the analytical replicates

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Table 1: Characteristic Masses (m/z) for Quantification

Compound Name	Abbreviation [1]	Chemical Formula	CAS No.	Primary Ion	Secondary Ion(s)
Methyl *tertiary*-butyl ether [2]	**MTBE**	**$C_5H_{12}O$**	**1634-04-4**	**73**	**43, 41, 39**
Ethyl *tertiary*-butylether	ETBE	$C_6H_{14}O$	637-92-3	59	87, 41, 57
Methyl *tertiary*-amylether	TAME	$C_6H_{14}O$	994-05-8	73	43, 55, 87
Acetone	na	C_3H_6O	67-64-1	43	42, 58, 39
tertiary-Butylformate [3]	TBF	$C_5H_{10}O_2$	762-75-4	59	41, 57, 39

na : not applicable

[1] Abbreviation – sometimes used in lieu of the full name in the analytical software.

[2] **MTBE is the only compound with data being reported by SOP MLD059.**

[3] NIST has found TBF unstable in gas cylinders. Therefore, NIST will not certify TBF concentrations in their standard cylinders.

Table 2: MLD059 Standards and Controls

Date Range	Standard Cylinder	Control Cylinder
7/1/02 – present	AAL053319	CC109953

Table 3: Thermal Zones for the Lotus Consulting/Varian Model 3800 Gas Chromatograph, with Cryogenic/Adsorbent Concentration System and ITD

Thermal Zone #	GC Injector/SPT or Valve Oven Status Label	GC Control Label	Workstation Method Label	Function
1	Front: 1079	Front 1079	Front Injector Type 1079	Cryogenic/Adsorbent Tap Temperature (Front Cold Trap)
2	Middle: 1079	Middle 1079	Middle Injector Type 1079	Cryofocuser Temperature (Middle Cold Trap)
3	Rear Valve Oven	Large Rear Valve Oven	Rear Valve Oven	SSV, Valve 1, and Valve 2 Heated Valve Oven Temperature
4	Middle Valve Oven	Large Rear Valve Oven	Middle Valve Oven	Sampling Manifold to SSV Line Heater Temperature
5	Front Valve Oven	Front Small Valve Oven	Front Valve Oven	Valve 3 and Valve 4 Heated Valve Oven Temperature

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Table 4: Function of Valves for the Lotus Consulting/Varian Model 3800 Gas Chromatograph, with a Cryogenic/Adsorbent Concentration System and ITD			
Valve/ Relay #	**Name**	**Relay Event and Description**	**Function**
1	Sample Valve (Valve 1)	– Off	Sample flow blocked; Internal Standard inlet to vent; N_2 dry purge flow through sample loop to Valve 2 (V2).
		+ On	Sample flow to Valve 2 (V2); Internal Standard inlet through sample loop to vent; N_2 dry purge flow to vent;
2	Sample Preconcentration Trap (Valve 2)	– Off	Flow from Valve 1 (V1) to MFC then vacuum; He trap purge flow through Cryogenic/Adsorbent Trap to Valve 3 (V3).
		+ On	Flow from Valve 1 through Cryogenic/Adsorbent Trap to MFC then vacuum; He trap purge flow to Valve 3 (V3).
3	Sample Preconcentration Trap (Valve 3)	– Off	Flow from Valve 2 (V2) to Valve 4 (V4); He column carrier flow to GC column.
		+ On	Flow from Valve 2 (V2) to vent; He column carrier flow to Valve 4 (V4) then to GC column.

Table 4: Function of Valves for the Lotus Consulting/Varian Model 3800 Gas Chromatograph, with a Cryogenic/Adsorbent Concentration System and ITD			
Valve/ Relay #	**Name**	**Relay Event and Description**	**Function**
4	Cryofocuser Isolation (Valve 4)	– Off	Flow from Valve 3 (V3) through Cryofocuser and back to Valve 3 (V3).
		+ On	Flow from Valve 3 (V3) and back to Valve 3 (V3); Cryofocuser Isolated.
5	Internal Standard (Valve 5)	– Off	Internal Standard inlet to Valve 1 (V1) blocked.
		+ On	Internal Standard inlet to Valve 1 (V1) opens.
6	Valve/Relay Event 6	– Off	No Action
		+ On	No Action
7	Valve/Relay Event 7	– Off	No Action
		+ On	No Action

Table 5: Thermal Zones for the Lotus Consulting/Varian Model 3800 Gas Chromatograph Configured as a Stand Alone Cryogenic/Adsorbent Concentration System

Thermal Zone #	GC Injector/SPT or Valve Oven Status Label	GC Control Label	Workstation Method Label	Function
1	Front: 1079	Front 1079	Front Injector Type 1079	Cryogenic/Adsorbent Tap Temperature (Front Cold Trap)
2	Middle: 1079	Middle 1079	Middle Injector Type 1079	Cryofocuser Temperature (Middle Cold Trap)
3	Rear Valve Oven	Rear Large Valve Oven	Rear Valve Oven	Sampling Manifold to SSV Line Heater Temperature
5	Middle Valve Oven	Middle Small Valve Oven	Middle Valve Oven	SSV, Valve 1, and Valve 2 Heated Valve Oven Temperature
6	Rear: 1041	Rear 1041	Rear Injector Type 1079	Valve 3 and Valve 4 Heated Valve Oven Temperature

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Table 6: Saturn ITD Autotune Evaluation Report

09:26:42 Auto Tune: Started
09:26:42 Air/Water Check: Started
09:27:06 Air Check: Acceptable Level Found (28 Width: 0.6 m/z)
09:27:07 Water Check: Acceptable Level Found (19/18 Ratio: 11.9 %)
09:27:07 Air/Water Check: Completed - No Problems Found

09:27:07 Integrator Zero Set: Started
09:27:12 Integrator Zero Set: Setting is OK (Setting: 142, Average Counts: 0.45)
09:27:12 Integrator Zero Set: Completed
09:27:12 Electron Multiplier: Started
09:27:13 Electron Multiplier: Offset Determined (Offset: 1 Count(s))
09:27:48 Electron Multiplier: Pre-Adjustment Successful (EM Voltage: 1900)
09:31:50 Electron Multiplier: Low Voltage End Found (EM Voltage: 1600)
09:33:12 Electron Multiplier: High Voltage Start Found (EM Voltage: 1800)
09:33:25 Electron Multiplier: Space Charge Adjusted (Target: 22000, Val/Iso: 0.21)
09:33:28 Electron Multiplier: Peak Threshold Met (Inten: 715 counts)
09:33:28 Electron Multiplier: 10^5 Gain setting is OK (EM Voltage: 1700)
09:33:29 Electron Multiplier: Final Gain setting is OK (EM Voltage: 1700)
09:33:29 Electron Multiplier: Completed
09:33:29 Auto Tune: Completed

09:35:28 Auto Tune: Started
09:35:28 RF Full Scale Adj: Started
09:35:37 RF Full Scale Adj: Centered on Mass 69 at 68.52 (Setting: 163)
09:35:42 RF Full Scale Adj: Centered on Mass 414 at 415.96 (Setting: 139)
09:35:46 RF Full Scale Adj: Centered on Mass 614 at 614.30 (Setting: 137)
09:35:47 RF Full Scale Adj: Setting is OK (Setting: 137, Mass: 614, Apex: 614.1)
09:35:47 RF Full Scale Adj: Completed
09:35:47 Multi-Point Mass Cal: Started
09:35:54 Multi-Point Mass Cal: Found Calibration Mass 28 at 27.78
09:36:01 Multi-Point Mass Cal: Found Calibration Mass 69 at 68.65
09:36:05 Multi-Point Mass Cal: Found Calibration Mass 131 at 130.59
09:36:17 Multi-Point Mass Cal: Found Calibration Mass 264 at 263.64
09:36:34 Multi-Point Mass Cal: Found Calibration Mass 414 at 413.80
09:36:54 Multi-Point Mass Cal: Found Calibration Mass 464 at 463.84
09:37:16 Multi-Point Mass Cal: Found Calibration Mass 502 at 501.80
09:37:43 Multi-Point Mass Cal: Found Calibration Mass 614 at 614.09
09:37:43 Multi-Point Mass Cal: Calibration is OK (Slope: 6.263, Std Dev: 0.046)
09:37:43 Multi-Point Mass Cal: Completed
09:37:43 Auto Tune: Completed

Table 7: Agilent MSD Autotune Evaluation Report

Instrument Name:	GC/MS Instrument #3 (HP6890/HP5973)	
DC Polarity:	Positive	
Filament:	1	
Basepeak should be 69 or 219		OK
Position of mass 69	69.00	OK
Position of mass 219	219.00	OK
Position of isotope mass 70	70.00	OK
Position of isotope mass 220	219.99	OK
Position of isotope mass 503	502.91	OK
Ratio of mass 70 to mass 69 (0.5 – 1.6%)	1.11	OK
Ratio of mass 220 to mass 219 (3.2 – 5.4%)	4.30	OK
Ratio of mass 503 to mass 502 (7.9 – 12.3%)	9.98	OK
Ratio of 219 to 69 should be >40% and is	66.88	OK
Ratio of 502 to 69 should be >2.4% and is	5.69	OK
Mass 69 Precursor (<= 3%)	0.08	OK
Mass 219 Precursor (<= 6%)	0.33	OK
Mass 502 Precursor (<= 12%)	3.32	OK
Testing for a leak in the system		
Ratio of 18 to 69 (<20%)	2.12	OK
Ratio of 28 to 69 (<10%)	2.67	OK
Electron Multiplier Voltage	1341	OK
Tune portion of system verification passed		

Table 8: Program Times, Relay #'s, and Status for the Lotus Consulting/-Varian Model 3800 Gas Chromatograph, with a Cryogenic/Adsorbent Concentration System and ITD		
Time (minutes)	**Relay # & Status**	**Events**
0.00	-1-2-3-4-5	All Valves are off (-): The sample flow is blocked and N_2 dry purge gas flows through the sample loop to Valve 2 (V2) then through the MFC to vacuum. The Internal Standard Valve 5 (V5) is off, and the Internal Standard inlet to Valve (1) is connected to vent. He trap purge gas flows through Valve 2 (V2), through the Cryogenic/Adsorbent Trap, through Valve 3 (V3), through Valve 4 (V4), through the Cryofocuser, back through Valve 3 (V3) to vent. He carrier gas flows through Valve 3 (V3) to the GC column.
0.01	**+1**-2-3-4-5	Valve 1 (V1) is turned on (**+1**): This allows the sample to flow through Valve 1 (V1), through Valve 2 (V2) then through the MFC to vacuum, purging the lines with new sample. The N_2 purge gas flow is sent to vent. The Internal Standard Valve 5 (V5) is off, and the Internal Standard inlet to Valve (1) is connected, through the sample loop to vent. He trap purge gas flows through Valve 2 (V2), through the Cryogenic/Adsorbent Trap, through Valve 3 (V3), through Valve 4 (V4), through the Cryofocuser, back through Valve 3 (V3) to vent. He carrier gas flows through Valve 3 (V3) to the column.
2.00	**+1+2**-3-4-5	Valve 2 (V2) is turned on (**+2**) and Valve 1 (V1) remains on (**+1**):

Table 8: Program Times, Relay #'s, and Status for the Lotus Consulting/-Varian Model 3800 Gas Chromatograph, with a Cryogenic/Adsorbent Concentration System and ITD		
Time (minutes)	**Relay # & Status**	**Events**
		This allows the sample to flow through Valve 1 (V1), through Valve 2 (V2), through the Cryogenic/Adsorbent Trap and then through the MFC to vacuum. The N_2 purge gas flow is sent to vent. ***This starts sample loading of the Cryogenic/-Adsorbent Trap.*** The Internal Standard Valve 5 (V5) is off, and the Internal Standard inlet to Valve (1) is connected, through the sample loop to vent. He purge gas flows through Valve 2 (V2), through Valve 3 (V3), through Valve 4 (V4), through the Cryofocuser, back through Valve 3 (V3) to vent. He carrier gas flows through Valve 3 (V3) to the column.
5.00	-1**+2**-3-4-5	Valve 1 (V1) is turned off (-1) and Valve 2 (V2) remains on (**+2**): The sample flow is blocked and N_2 purge gas flows through the loop to Valve 2 (V2), through the cryogenic/-adsorbent trap and then through the MFC to vacuum. This flushes the loop and any sample remaining in the lines, and does a "dry" purge of the to the cryogenic/-adsorbent trap. ***This terminates sample loading of the cryogenic/-adsorbent trap.*** The Internal Standard Valve 5 (V5) is off, and the Internal Standard inlet to Valve (1) is connected, through the sample loop to vent. He purge gas flows through Valve 2 (V2), through Valve

Table 8: Program Times, Relay #'s, and Status for the Lotus Consulting/-Varian Model 3800 Gas Chromatograph, with a Cryogenic/Adsorbent Concentration System and ITD		
Time (minutes)	**Relay # & Status**	**Events**
		3 (V3), through the cryofocuser, back through Valve 3 (V3) to vent. He carrier gas flows through Valve 3 (V3) to the column. ***Note: The sample volume is varied by controlling the action of Valve 1 (V1).***
8.00	-1-2-3-4-5	Valve 2 (V2) is turned off (-2): The sample flow is blocked and N_2 dry purge gas flows through the sample loop to Valve 2 (V2) then through the MFC to vacuum. The Internal Standard Valve 5 (V5) is off, and the Internal Standard inlet to Valve (1) is connected to vent. He trap purge gas flows through Valve 2 (V2), through the Cryogenic/Adsorbent Trap, through Valve 3 (V3), through Valve 4 (V4), through the Cryofocuser, back through Valve 3 (V3) to vent. ***This starts the transfer of the cryotrap contents to the cryofocuser.*** He carrier gas flows through Valve 3 (V3) to the column.
11.00	-1-2-3**+4**-5	Valve 4 (V4) is turned on (**+4**): The sample flow is blocked and N_2 dry purge gas flows through the sample loop to Valve 2 (V2) then through the MFC to vacuum. The Internal Standard Valve 5 (V5) is off, and the Internal Standard inlet to Valve (1) is connected to vent. He trap purge gas flows through Valve 2 (V2), through

Table 8: Program Times, Relay #'s, and Status for the Lotus Consulting/-Varian Model 3800 Gas Chromatograph, with a Cryogenic/Adsorbent Concentration System and ITD		
Time (minutes)	**Relay # & Status**	**Events**
		the Cryogenic/Adsorbent Trap, through Valve 3 (V3), through Valve 4 (V4), back through Valve 3 (V3) to vent. ***This terminates the transfer of the cryotrap contents to the cryofocuser, and isolates the cryofocuser for pre-heating.*** He carrier gas flows through Valve 3 (V3) to the column.
12.00	-1-2**+3**-4**+5**	Valves 3 is turned on (**+3**) and Valve 4 (V4) is turned off (-4), and Relay 5 (V5) is turned on (**+5**): The sample flow is blocked and N_2 dry purge gas flows through the sample loop to Valve 2 (V2) then through the MFC to vacuum. The Internal Standard Valve 5 (V5) is off, and the Internal Standard inlet to Valve (1) is connected to vent. He trap purge gas flows through Valve 2 (V2), through the Cryogenic/Adsorbent Trap, through Valve 3 (V3) to vent. He carrier gas flows through Valve 3 (V3), through the cryofocuser, back through Valve 3 (V3) to the GC column. ***This starts backflushing the cryofocuser contents to GC column.***
14.00	-1-2-3-4-5	All Valves are off (-): The system is returned to the state a time 0.00.

Table 9: Precision Measurements for MLD059

Dates	MTBE (ppb)
6/13/02	4.455
6/13/02	4.239
6/13/02	4.164
6/13/02	4.270
6/13/02	3.972
6/13/02	4.297
6/18/02	4.316
6/18/02	4.188
6/18/02	4.522
6/18/02	4.841
6/20/02	4.487
6/24/02	4.538
6/24/02	5.098
6/25/02	4.432
6/25/02	4.658
6/25/02	4.512
6/25/02	4.451
6/26/02	4.236
7/2/02	4.886
7/3/02	5.030
7/3/02	5.143
7/3/02	5.070
7/3/02	4.942

Dates	MTBE (ppb)
7/5/02	4.224
7/5/02	4.789
7/5/02	4.834
7/5/02	4.440
7/8/02	4.028
7/8/02	4.371
7/8/02	4.449
7/8/02	4.210
Mean:	4.52
Standard Deviation (SD):	0.328
%Relative Standard Deviation (%RSD):	7.25
Upper Control Limit (UCL):	5.50
Upper Warning Limit (UWL):	5.17
Lower Warning Limit (LWL):	3.86
Lower Control Limit (UCL):	3.54

UCL = Mean + (3 * SD)
UWL = Mean + (2 * SD)
LWL = Mean - (2 * SD)
LCL = Mean - (3 * SD)

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Figure 1: Standby/Ready/Idle

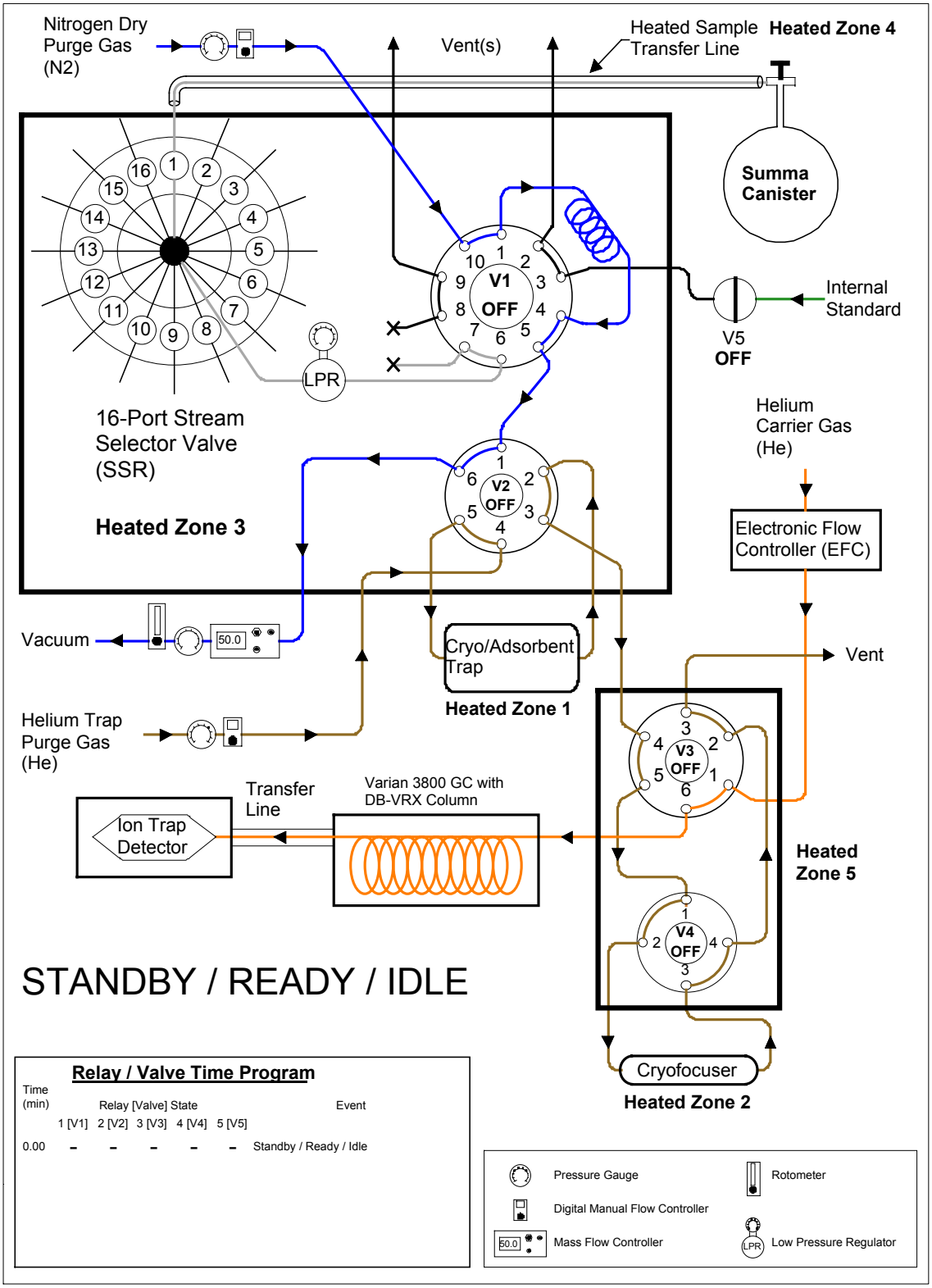


Figure 2: Purge Sample Line

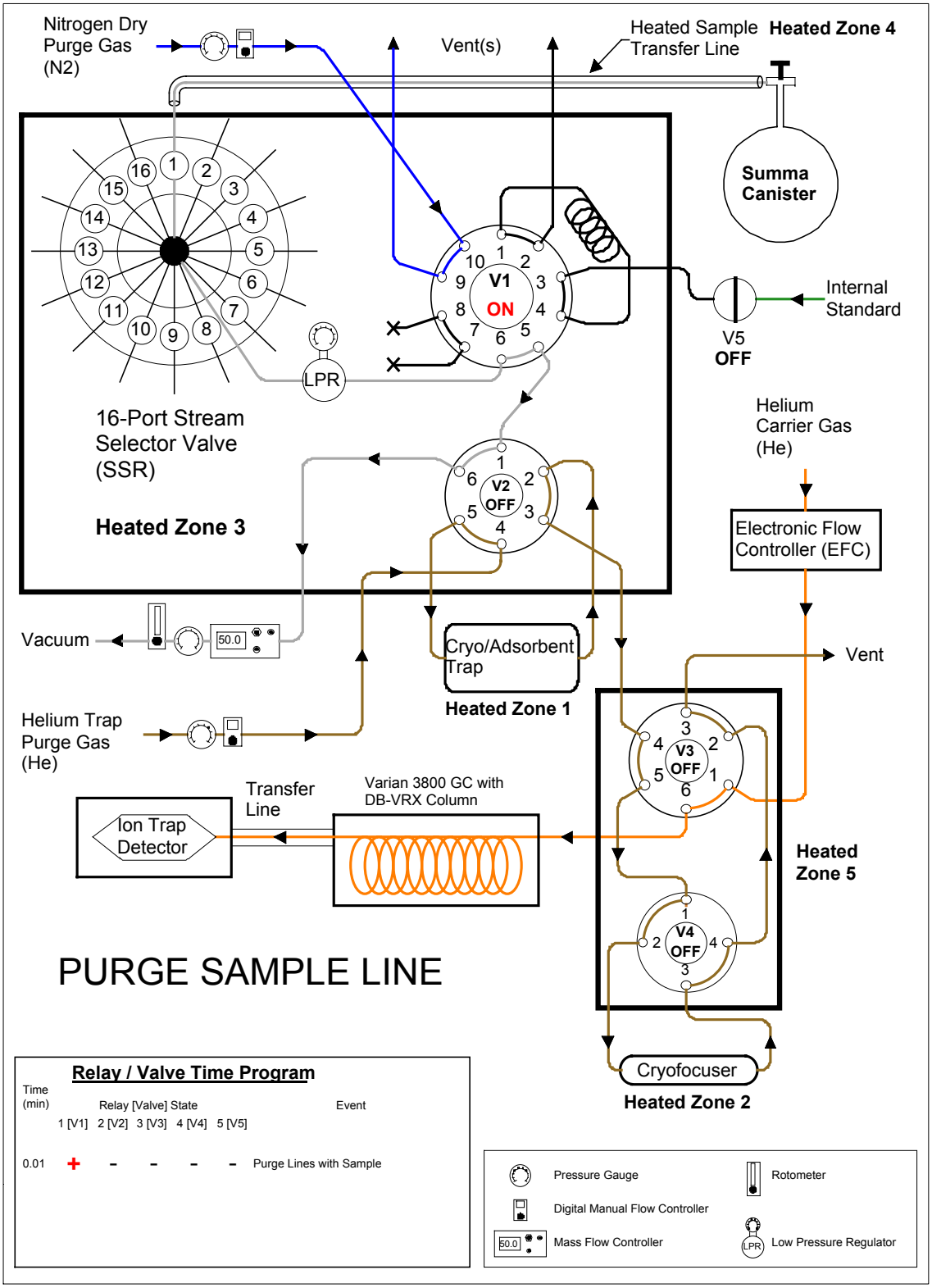


Figure 3: Load Adsorbent Trap

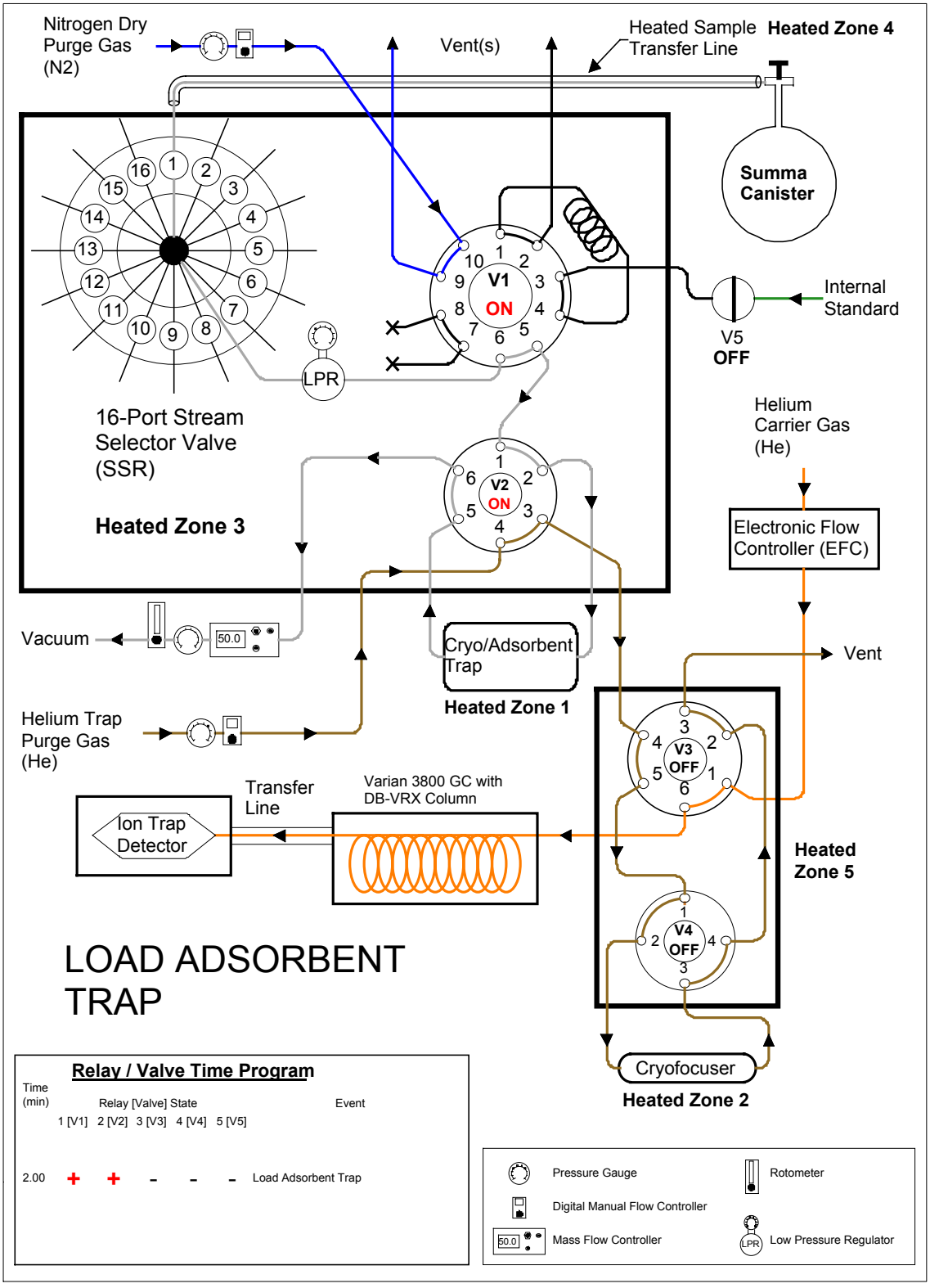


Figure 4: Flush Adsorbent Trap

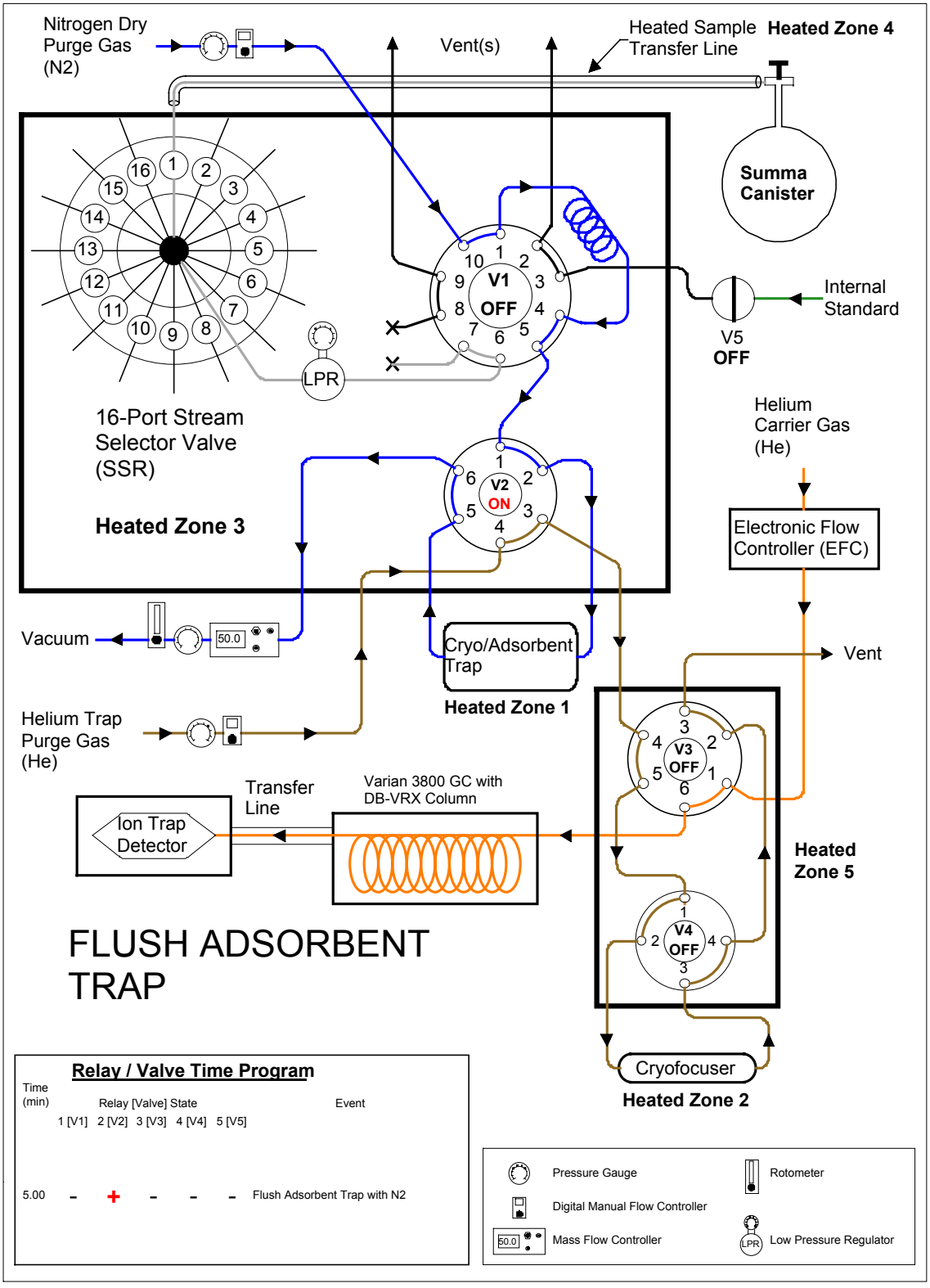


Figure 5: Transfer to Cryofocuser

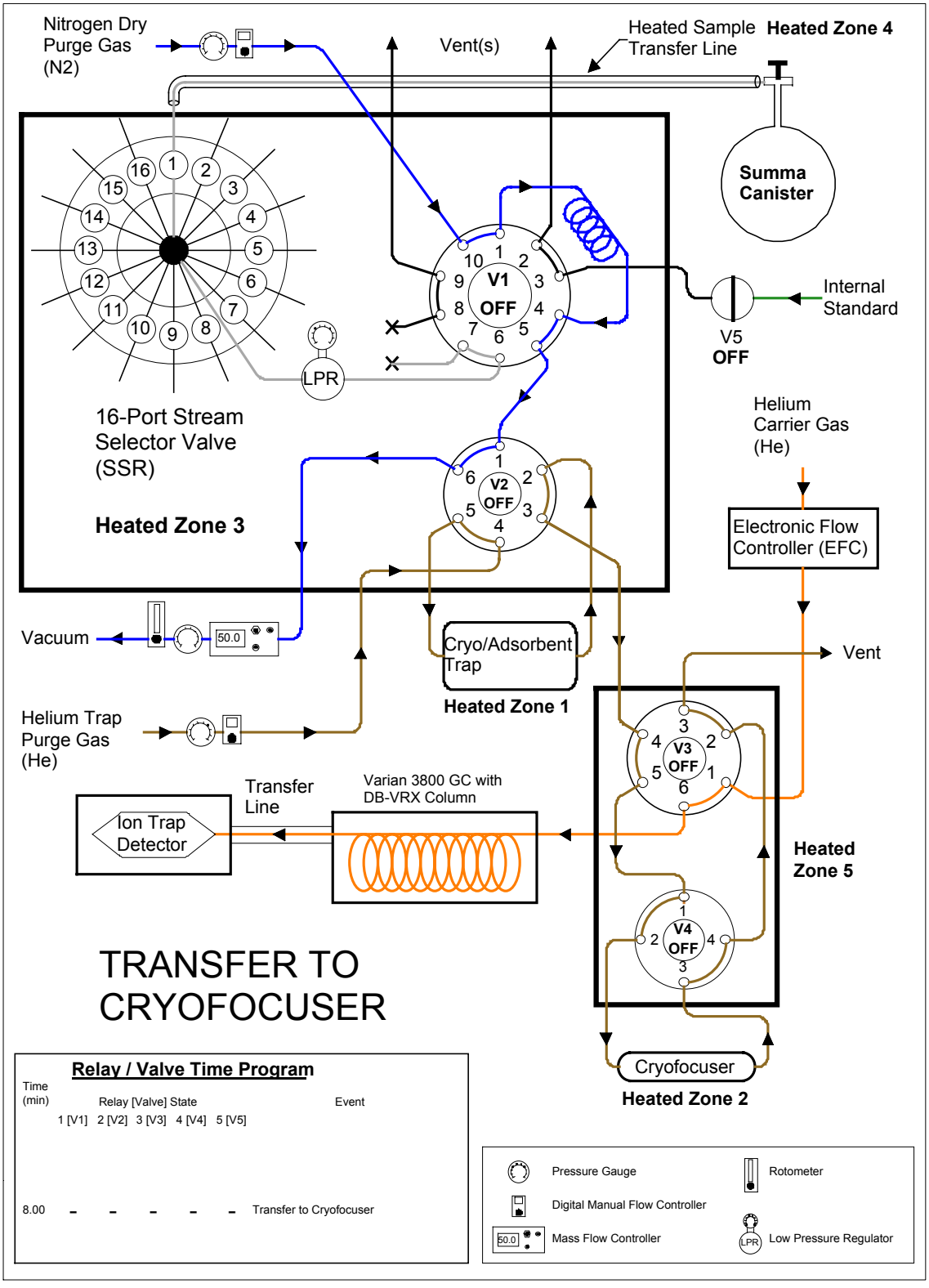


Figure 6: Isolate Cryofocuser

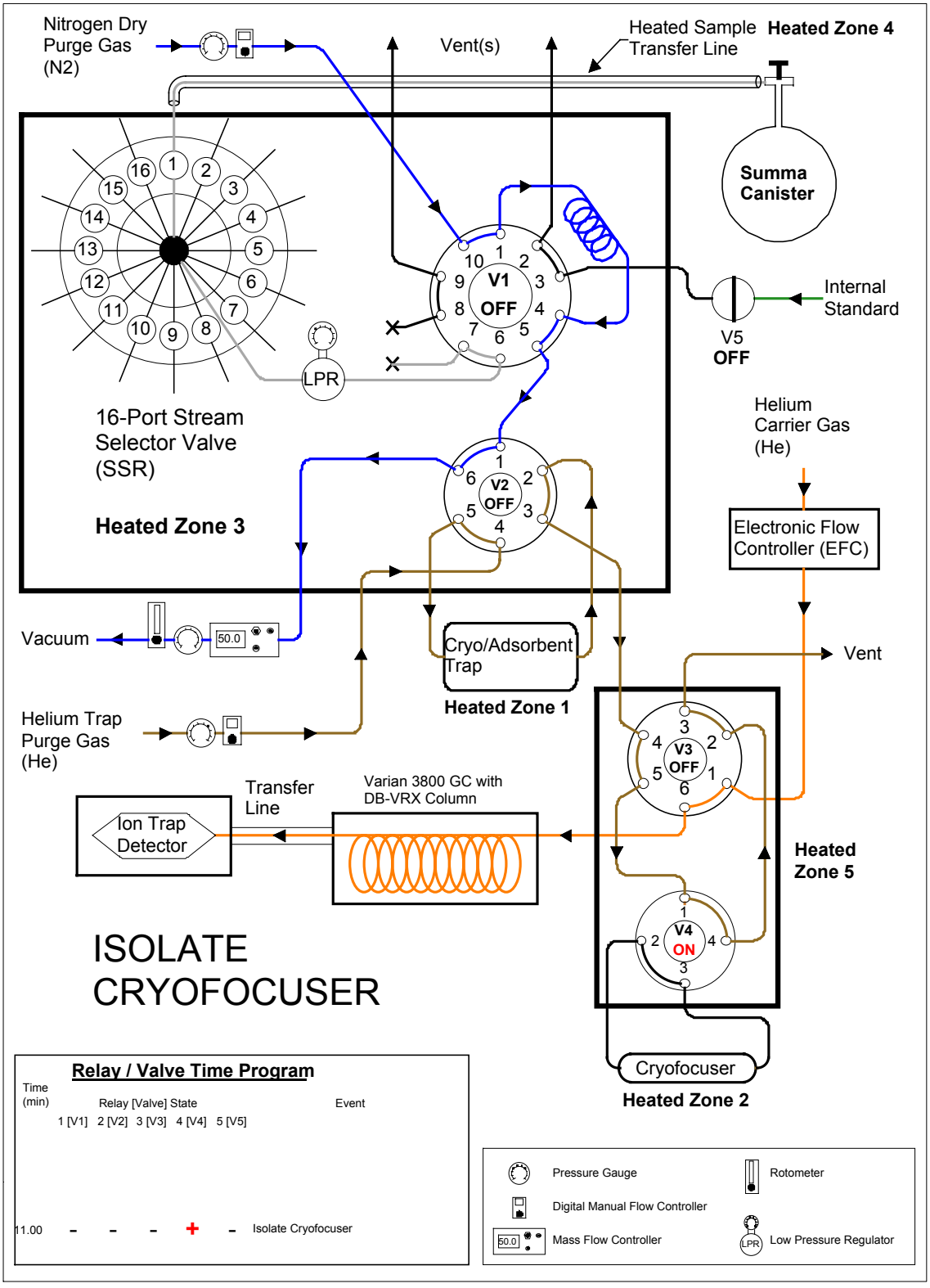


Figure 7: Desorb Cryofocuser

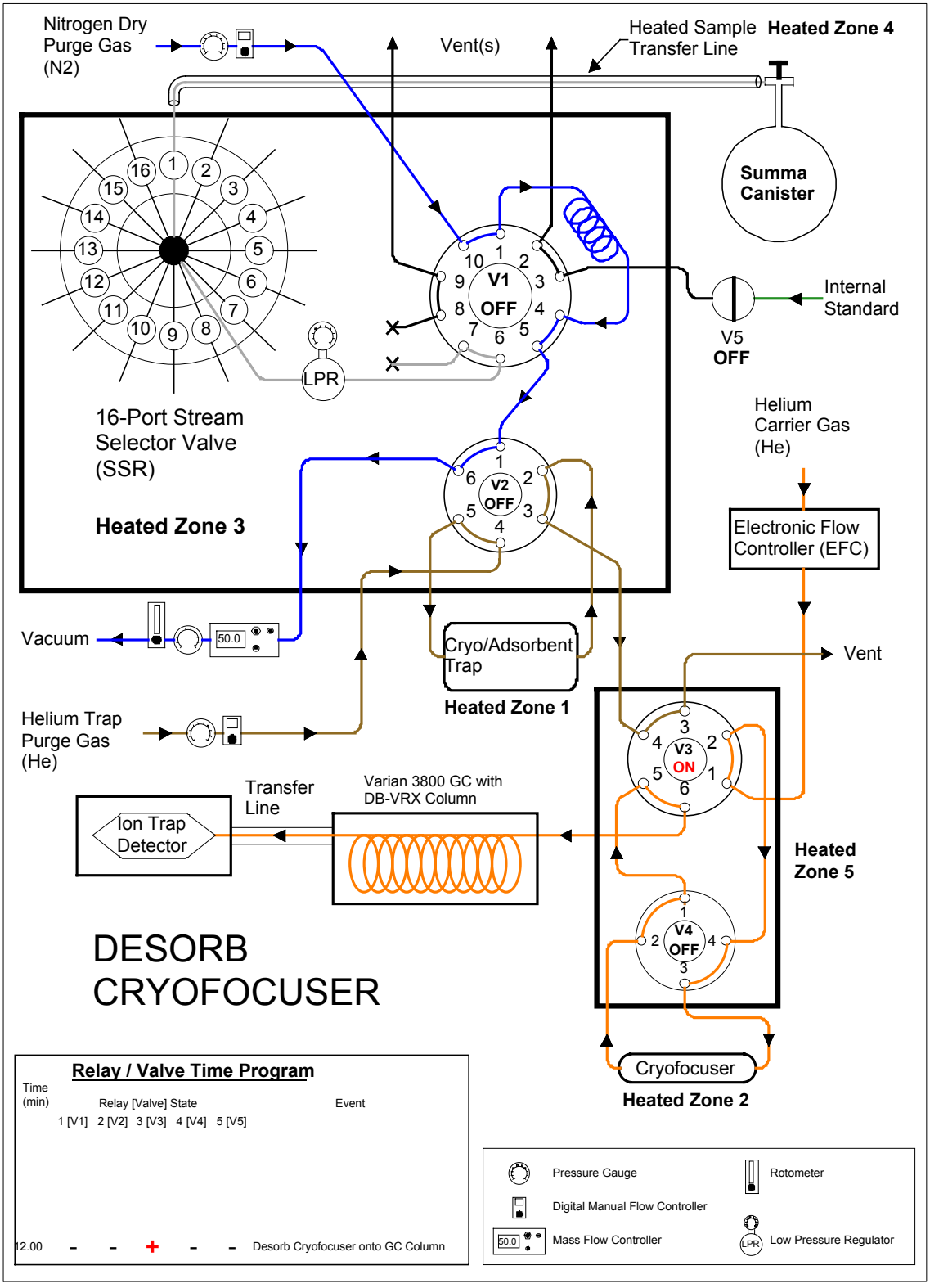


Figure 8: Concentrator Programming Sequence

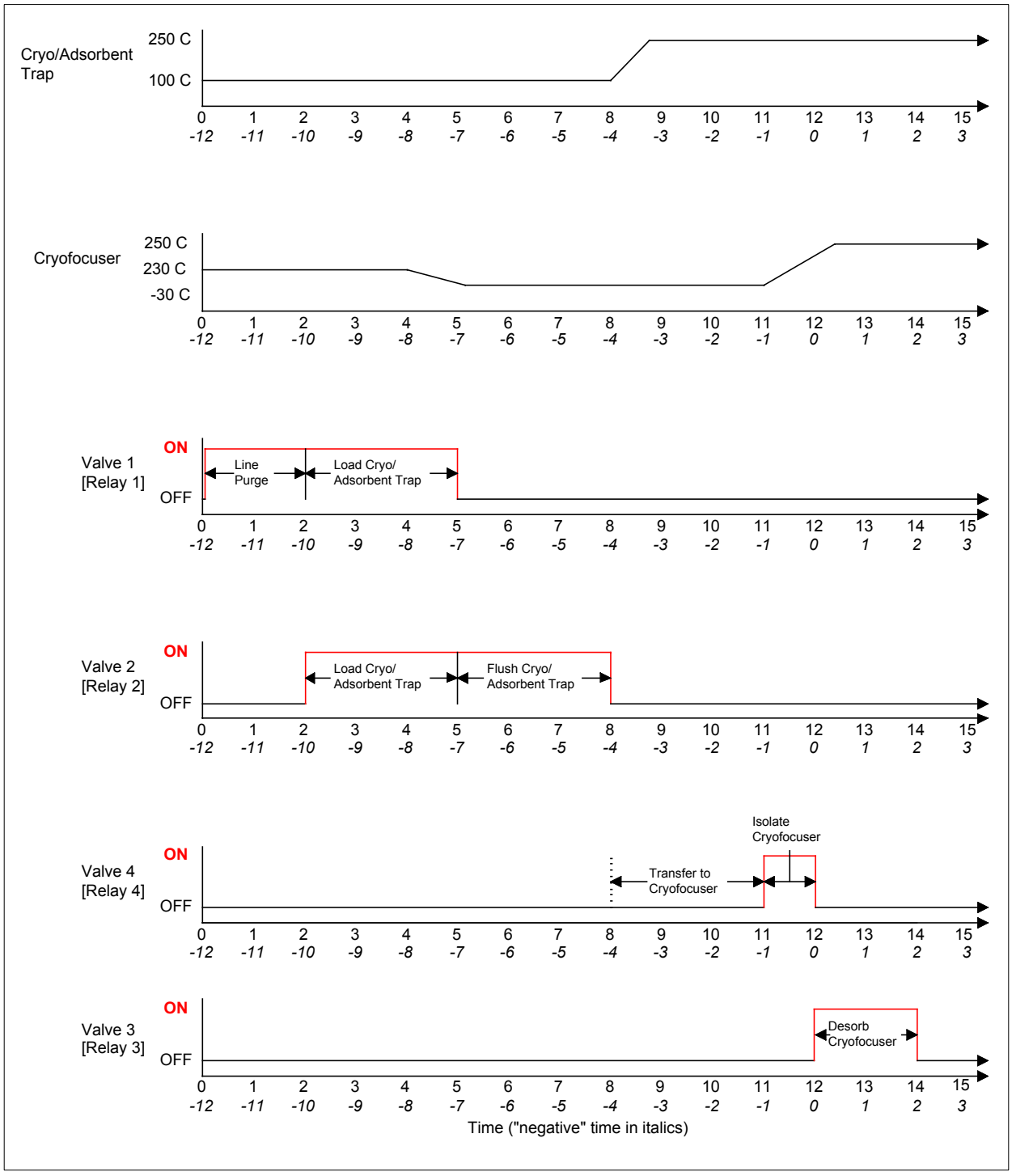


Figure 9: Typical Calibration Standard TIC

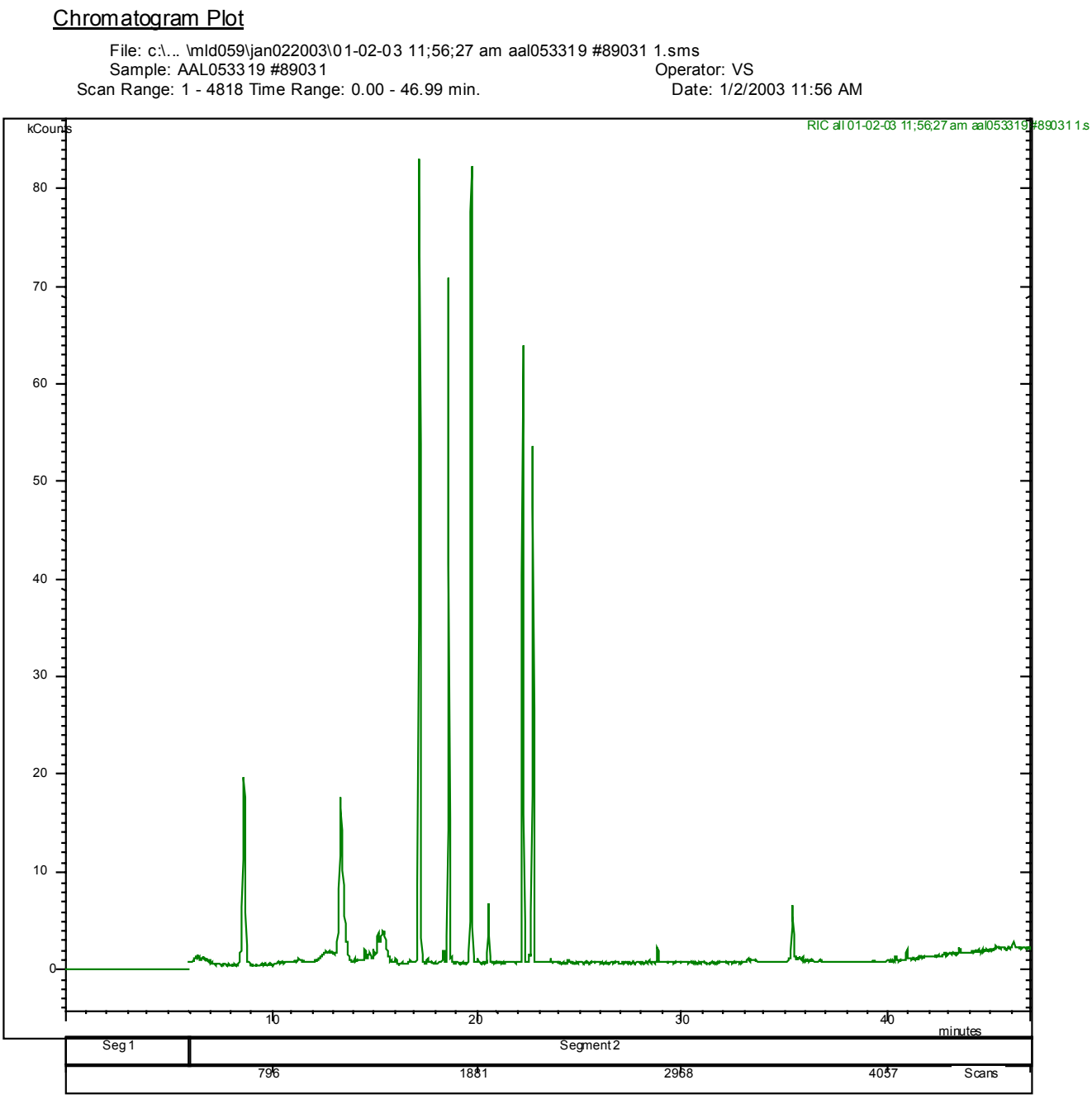


Figure 10: Typical Ambient Air TIC

Chromatogram Plot

File: c:\... \data\mld059\jan022003\01-02-03 03;01;30 pm tx004983 lb 1.sms
Sample: TX004983 LB
Scan Range: 1 - 4815 Time Range: 0.00 - 46.99 min.

Operator: VS
Date: 1/2/2003 3:01 PM

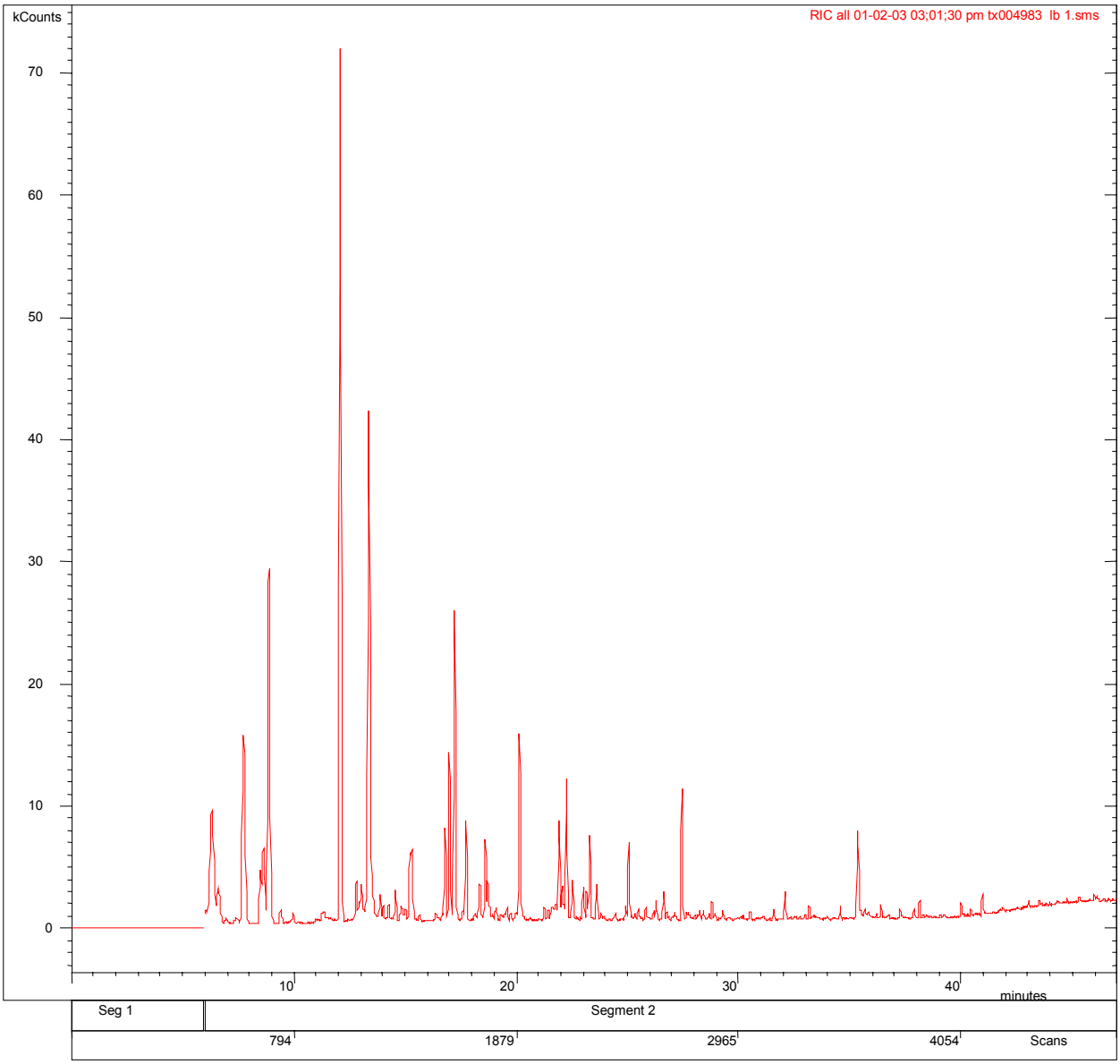
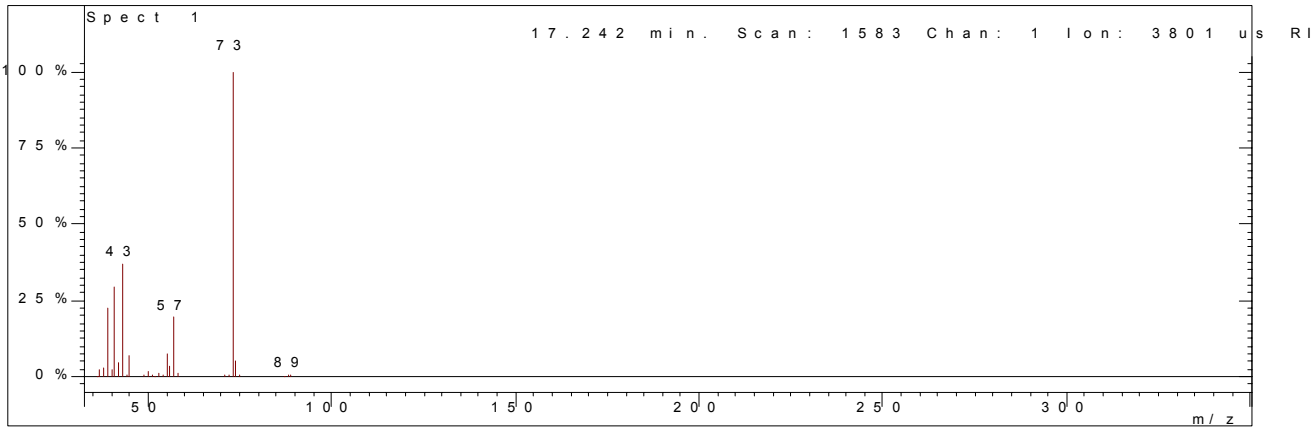


Figure 11: Typical Mass Spectrum

Scan 1583 from c:\... \01-02-03 11;56;27 am aal053319 #89031 1.sms



Spectrum from c:\... 01-02-03 11;56;27 am aal053319 #89031 1.sm
Scan No: 1583, Time: 17.242 minutes
No averaging. Background corrected.
Comment: 17.242 min. Scan: 1583 Chan: 1 Ion: 3801 us RIC: 82627 BC
Pair Count: 28 MW: 0 Formula: None CAS No: None Acquired Range: 33 -

Figure 12: MTBE Control Chart

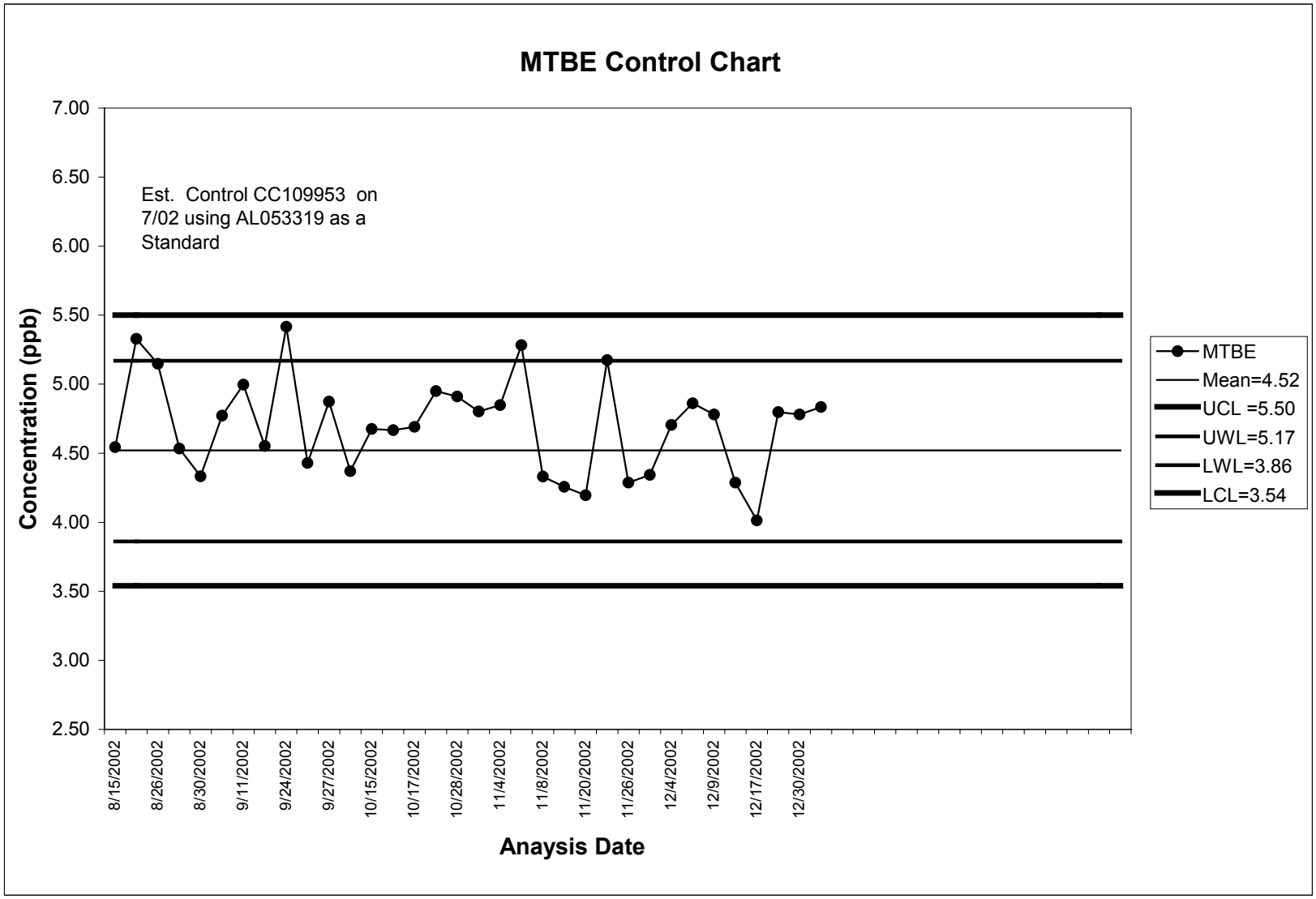
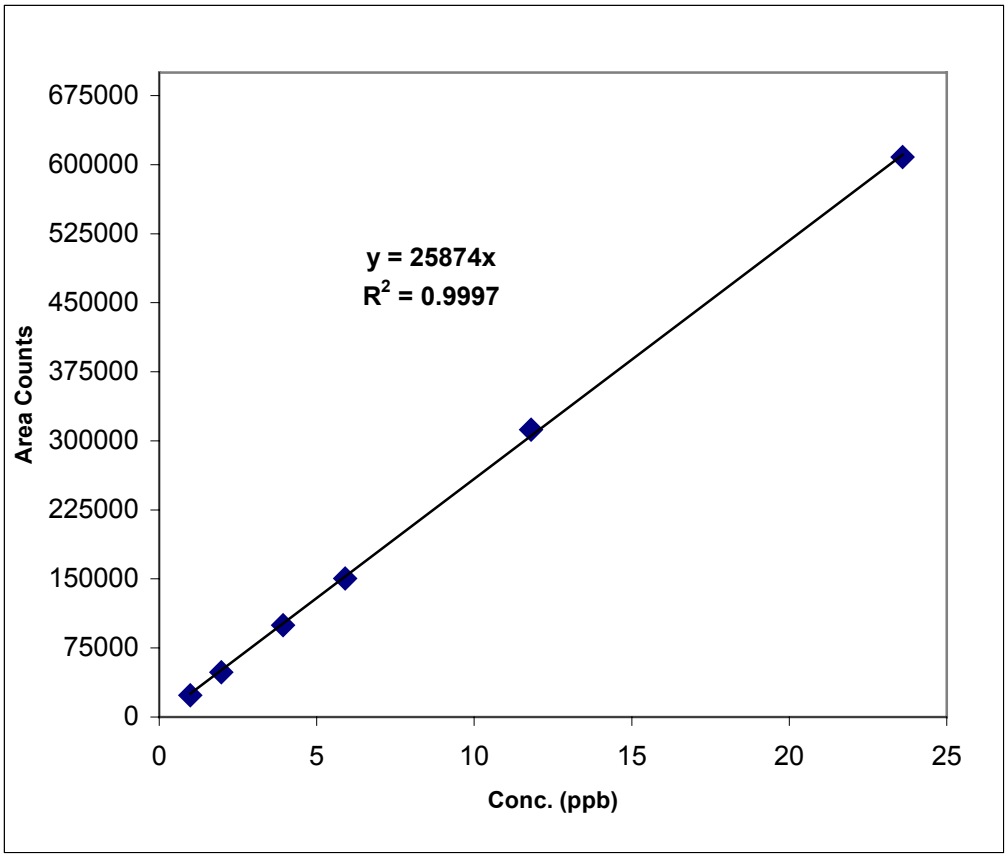


Figure 13: Methyl *tert*-Butyl Ether Multipoint Analysis (6/22/02)

MTBE 5.90 ppb

LEVELS OF CONCENTRATION (PPB)						
cc	**25**	**50**	**100**	**150**	**300**	**600**
ppb	**0.98**	**1.97**	**3.93**	**5.90**	**11.80**	**23.60**
1st Run	24014	49659	95608	151781	317279	606268
2nd	24427	48822	101434	155323	308660	591651
3rd	22875	47755	102495	144480	310191	627138
Mean=	23772	48745	99846	150528	312043	608352
Std.Dev.=	804	954	3708	5529	4598	17835
%RSD=	3.4	2.0	3.7	3.7	1.5	2.9
# Obs. =	3	3	3	3	3	3



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Appendix I: MLD059 Standard and Control Concentrations

	Abbreviation [1]	NIST (Standard) ALM053319 ppbv	Scott-Marin (Control) CC109953 ppbv [2]	ppbv
Methyl *tertiary*-butyl ether [3]	**MTBE**	**5.9 ± 0.3**	**4.52**	**5.0 [4]**
Ethyl *tertiary*-butylether	ETBE	5.9 ± 0.3	na	5.0 [4]
Methyl *tertiary*-amylether	TAME	4.4 ± 0.2	na	5.0 [4]
Acetone	na	10.5 ± 0.5	na	10 [4]
Tertiary-Butylformate [5]	TBF	2.5 ± 0.3	na	na
Ethanol	EtOH	26.4 ± 1.3	na	20 [4]
Hexane	HEX	7.4 ± 0.3	na	4.8 ± 1.0
Benzene	BENZ	6.0 ± 0.2	na	5.3 ± 1.1

na: not applicable

(1) Abbreviation – sometimes used in lieu of the full name in the analytical software

(2) Control concentrations as determined by Method MLD059

(3) MTBE is the only compound with data being reported by SOP MLD059.

(4) Uncertified concentrations as received from the vendor.

(5) NIST has found TBF unstable in gas cylinders. Therefore, NIST will not certify TBF concentrations in their standard cylinders.

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Appendix II: Saturn GC/MS Workstation

A Varian Saturn GC/MS Workstation includes an Intel compatible PC, an Ethernet network adapter, Microsoft 9.X, NT 4.0, or newer, operating system, and Varian Saturn Workstation software, Version 5.52 or newer. The GC/MS Workstation automates control of the integrated Varian/Lotus Cryogenic/Adsorbent Concentration system, the Varian Model 3800 Gas Chromatograph, and the Varian Model 2000 Ion Trap Detector (ITD). This automation covers:

- Concentration of the sample;
- Introduction of the concentrated sample onto the GC column;
- Set points for the GC carrier gas flow and the temperature of the GC column oven, the concentrator heated zones 1 through 5, and the GC to ITD transfer line
- All operating and data acquisition parameters of the ITD.

This software is also used for the analysis and reporting of the acquired MS data. For a more detailed discussion of the Workstation software, including setting up methods, sequences, and sample lists, and data analysis, refer to the following manual on CD-ROM:

- “Varian Saturn GC/MS Workstation – System Software”, Version 5.52, by Varian, Inc. (P/N 03-910876-01)

Additional resources by Randall Bramston-Cook of Lotus Consulting are:

- “Ultra Trace Hydrocarbon System Operator’s Manual”
- “Stream Selector Valve Control Software for Varian Workstation Operator’s Manual”
- "Varian GC Star Workstation Manual"

The instrument setpoints are stored on the Workstation as methods. Method MTBE.mth is used for normal operation and data acquisition. Method IDLE.mth is used for system standby. Both methods are used in automated sequences. Method MTBEQUANT.mth has data handling and reporting sections. It is used for identification, quantitation, and reporting of the data.

Copies of the Varian Saturn Workstation acquisition, idle, and data processing methods are listed on the following pages. Sections that are not used in a particular method are shown in lighter type. Screen shots of Additional Temperature Settings, the Sample List, and the Sequence List are also shown.

Appendix II - Saturn GC/MS Workstation Method - MTBE.MTH

****
Saturn GC/MS Workstation - Method Listing Tue Jan 14 10:35:43 2003
Method: MTBE.mth
****
****
Notes
****

HEATED ZONES:
Zone 1: Large Concentrator Trap; "Front 1079 Injector" Temp range -30 t o 250 C
Zone 2: Small Concentrator Trap; "Middle 1079 Injector" Temp range –30 to 250 C
Zone 3: Valves 1 and 2; "Rear Valve Oven" Temp. 80 C
Zone 4: FID - Not used
Zone 5: Valves 3 and 4; "Front Valve Oven" Temp. 150 C
Zone 6: Heated Sample Lines; "Middle Valve Oven" Temp 62 C

MS METHOD SECTION REPORT
Last Modified: 11/26/02 10:23 AM

Security Options Required:	EI
Mass Data Type:	CENTROID
Method Start Time:	-12.00 minutes
Number Of Segments:	2
Flow Sampling Segment:	
Start Time:	-8.00 minutes
End Time:	-5.00 minutes
Sample Flow Rate:	50 milliliters/minute
Segment Number 1:	
Description:	Filament Delay
Last Modified:	08/28/02 09:46 AM
Emission Current:	10 microamps
Mass Defect:	0 mmu/100u
Count Threshold:	1 counts
Multiplier Offset:	0 volts
Cal Gas:	OFF
Scan Time:	1.000 seconds
Segment Start Time:	0.00 minutes
Segment End Time:	6.00 minutes
Segment Low Mass:	40 m/z
Segment High Mass:	650 m/z
Ionization Mode:	NONE
Ion Preparation Technique:	NONE

No Ionization Mode
No Ion Preparation
Segment Number 2:

Description: Data Collection
Last Modified: 11/26/02 10:23 AM
Emission Current: 30 microamps
Mass Defect: 0 mmu/100u
Count Threshold: 1 counts
Multiplier Offset: 0 volts
Cal Gas: OFF
Scan Time: 0.620 seconds
Segment Start Time: 6.00 minutes
Segment End Time: 47.00 minutes
Segment Low Mass: 33 m/z
Segment High Mass: 350 m/z
Ionization Mode: EI AGC
Ion Preparation Technique: NONE

EI-Auto Mode:

Maximum Ionization Time: 25000 microseconds

	Mass Range	Ion. Storage Level	Ion. Time Factor
Scan Segment 1:	10 to 99	32.0 m/z	100%
Scan Segment 2:	100 to 249	32.0 m/z	100%
Scan Segment 3:	250 to 399	32.0 m/z	100%
Scan Segment 4:	400 to 650	32.0 m/z	100%

Target TIC: 20000 counts
Prescan Ionization Time: 100 microseconds
Background Mass: 33 m/z
RF Dump Value: 650.0 m/z

No Ion Preparation

MS REPORT FORMAT METHOD

PRINT OPTIONS:

Single-Run Reports:

Sample Report: Saturn A - Method MLD059 - MTBE
Printed Sample Report: Yes
ASCII Sample Report: No

Header Configuration:

Header Description:
Sample ID Operator
Instrument ID Data File
Acquisition Date Method
Calculation Date Header Time Date
Last Calibration
Inj. Sample Notes

Compound Report: Saturn A - Method MLD059 - MTBE
Printed Compound Reports: Yes
Analysis Samples: Yes
Verification Samples: No

Calibration Samples: No
Header Configuration:
Header Description:
Sample ID Operator
Instrument ID Data File
Sample Type Method
Measurement Type Calibration Type
Acquisition Date Last Calibration
Calculation Date
Inj. Sample Notes
Printout Scheduling: after sample list completion
Multi-Run Block Reports:
Calibration Reports:
Printed Block Report: No
ASCII Block Report: No
Printed Curve Report: No
Sample List Reports:
Print Summary Report: Yes
ASCII Summary Report: No
Print Control Charts: No
Print Control Charts: No
ASCII Reports Column Separator:
Use list separator in regional settings
Number of copies to print: 1
Number of decimal digits for amounts: 3
RESULTS FORMAT:
Results Table Format:
STANDARD
Show Ion Ratio Information: No
Show Compound Group Totals: Yes
Run Documentation:
Acquisition Segment Information: No
Run Log: Yes
Error Log: Yes
Calibration Report: Yes
Revision Log: Yes
Sample Notes: Yes
Method Notes: Yes
CHROMATOGRAM FORMAT:
Time Scale:
Start Time: 12.00 minutes
End Time: 24.00 minutes
Number of Plots: 1
Overlap Seconds: 3
Amplitude Scale:

Autoscale (Zoom Factor = 1.00)
Percentage of Offset = 5%
Plot Annotation:
General:
Acquisition Segments: Yes
Integration Events + Baselines: Yes
Peak Annotation:
RetentionTime: Yes
Scan Number: No
Compound Name: Yes
Compound Number: No
Peak Types to Annotate:
Identified: Yes
Failed: Yes
Missing: Yes
TIC's: No
Unknowns: No
Duplicates: No
COMPOUND REPORTS:
Target Compounds:
Results:
Type: STANDARD
Acquisition Segment Info: Yes
Target Plots:
Quan Ion Chromatogram Sample Spectrum
Reference Spectrum
Qualifier Ion Chromatograms
Unidentified Peaks:
Results:
Type: STANDARD
Acquisition Segment Info: Yes
Library Searched Plots:
Quan Ion Chromatogram Sample Spectrum
First Library Match Spectrum
Difference (Sample - 1st Match)
Plots Not Library Searched:
Quan Ion Chromatogram
CALIBRATION BLOCK REPORT:
Block Report:
Type: STANDARD
Title: Calibration Block Report
Curve Report:
Number of Curves/Page: 4
Show Outliers on Curve: Yes
Title: Calibration Curves Report

Appendix II - Saturn GC/MS Workstation Method - MTBE.MTH

SAMPLE LIST REPORTS:
- Include Run Types:
  - Calibration: Yes
  - Analysis: Yes
  - Verification: Yes
- Sort By:
  - First Key: Compound
  - Group By: First Key
- Summary Report:
  - Title: Summary Report
  - Summarize:
    - Retention Time: Yes
  - Results (Amount): Yes
    - Area: No
    - Height: No
- Control Charts:
  - Title: Control Chart
  - Chart: Retention Time
  - Control Limits: +/-2 Standard Deviations
  - Plot Options:
    - Number of Plots/Page: 4

****
3800 GC
****
Module Address: 44

Front Valve Oven
- Oven Power: On
- Temperature: 150 C

Middle Valve Oven
- Oven Power: On
- Temperature: 62 C

Rear Valve Oven
- Oven Power: On
- Temperature: 80 C

Valve Table
- Valve 1: Sample Valve
  - Initial: Off
  - 0.01 min: On
  - 2.00 min: On
  - 5.00 min: Off
  - 8.00 min: Off
  - 11.00 min: Off
  - 12.00 min: Off
  - 14.00 min: Off

Valve 2: Sample Valve
Initial: Off
0.01 min: Off
2.00 min: On
5.00 min: On
8.00 min: Off
11.00 min: Off
12.00 min: Off
14.00 min: Off

Valve 3: Sample Valve
Initial: Off
0.01 min: Off
2.00 min: Off
5.00 min: Off
8.00 min: Off
11.00 min: Off
12.00 min: On
14.00 min: Off

Valve 4: Sample Valve
Initial: Off
0.01 min: Off
2.00 min: Off
5.00 min: Off
8.00 min: Off
11.00 min: On
12.00 min: Off
14.00 min: Off

Valve 5: Internal Standard Valve
Initial: Off
0.01 min: Off
2.00 min: Off
5.00 min: Off
8.00 min: Off
11.00 min: Off
12.00 min: Off
14.00 min: Off

Front Injector Type 1079
Oven Power: On
Coolant: On
Enable Coolant at: 250 C
Coolant Timeout: 30.00 min

Temp (C)	Rate (C/min)	Hold (min)	Total (min)
100	0	8.00	8.00
250	200	50.25	59.00

Appendix II - Saturn GC/MS Workstation Method - MTBE.MTH

Middle Injector Type 1079

Oven Power:	On
Coolant:	On
Enable Coolant at:	250 C
Coolant Timeout:	20.00 min

Temp (C)	Rate (C/min)	Hold (min)	Total (min)
200	0	4.00	4.00
-30	200	5.85	11.00
250	200	46.60	59.00

Rear Injector EFC Type 3

Flow (ml/min)	Rate (ml/min	Hold (ml/min)	Total (min)
1.2	0.0	51.00	51.00
2.0	2.0	7.60	59.00

Column Oven

Coolant:	On
Enable Coolant at:	50 C
Coolant Timeout:	20.00 min
Stabilization Time:	0.10 min

Temp (C)	Rate (C/min)	Hold (min)	Total (min)
100	0.0	7.00	7.00
-10	100.0	4.40	12.50
200	5.0	4.50	59.00

Front FID Detector

Oven Power:	Off
Temperature	60 C
Electronics:	Off
Time Constant:	Fast

Time (min)	Range	Autozero
Initial	12	yes

Front Type 11 Detector EFC

Make up Flow:	0 ml/min
H2 Flow:	0 ml/min
Air Flow:	0 ml/min

Output Port A

Time (min)	Signal Source	Attenuation
Initial	Front	1

Output Port B

Time (min)	Signal Source	Attenuation
Initial	Front	1

Output Port C

Time (min)	Signal Source	Attenuation
Initial	Front	1

Data Acquisition

Detector Bunch Rate:	4 points (10.0 Hz)
Monitor Length:	64 bunched points (6.4 sec)
Front FID/TSD Scale:	1 Volts
Middle FID/TSD Scale:	1 Volts
Rear FID/TSD Scale:	1 Volts

*******End of Method**************************

Appendix II - Saturn GC/MS Workstation Method - IDLE.MTH

****

Saturn GC/MS Workstation - Method Listing Tue Jan 14 11:08:55 2003
Method: idle-check.mth

****

****

Notes

****

MS METHOD SECTION REPORT

Last Modified: 03/11/02 11:09 AM

Security Options Required: EI
Mass Data Type: CENTROID
Method Start Time: 0.00 minutes
Number Of Segments: 6

Segment Number 1:

Description:	Air/Water
Last Modified:	03/11/02 11:09 AM
Emission Current:	10 microamps
Mass Defect:	0 mmu/100u
Count Threshold:	1 counts
Multiplier Offset:	0 volts
Cal Gas:	OFF
Scan Time:	0.500 seconds
Segment Start Time:	0.00 minutes
Segment End Time:	0.50 minutes
Segment Low Mass:	10 m/z
Segment High Mass:	45 m/z
Ionization Mode:	EI Fixed

Ion Preparation Technique: NONE
EI-Fixed Mode:
Maximum Ionization Time: 25000 microseconds

	Mass Range	Ion. Storage Level	Ion. Time Factor
Scan Segment 1:	10 to 99	10.0 m/z	100%
Scan Segment 2:	100 to 249	10.0 m/z	100%
Scan Segment 3:	250 to 399	10.0 m/z	100%
Scan Segment 4:	400 to 650	10.0 m/z	100%

Ionization Time: 100 microseconds
No Ion Preparation.

Segment Number 2:

Description:	HMN/Background
Last Modified:	11/01/00 03:37 PM
Emission Current:	10 microamps
Mass Defect:	0 mmu/100u

Count Threshold: 1 counts
Multiplier Offset: 0 volts
Cal Gas: OFF
Scan Time: 0.870 seconds
Segment Start Time: 0.50 minutes
Segment End Time: 1.00 minutes
Segment Low Mass: 50 m/z
Segment High Mass: 650 m/z
Ionization Mode: EI AGC
Ion Preparation Technique: NONE
EI-Auto Mode:
Maximum Ionization Time: 25000 microseconds

	Mass Range	Ion. Storage Level	Ion. Time Factor
Scan Segment 1:	10 to 99	35.0 m/z	100%
Scan Segment 2:	100 to 249	35.0 m/z	100%
Scan Segment 3:	250 to 399	35.0 m/z	100%
Scan Segment 4:	400 to 650	35.0 m/z	100%

Target TIC: 20000 counts
Prescan Ionization Time: 100 microseconds
Background Mass: 45 m/z
RF Dump Value: 650.0 m/z
No Ion Preparation.

Segment Number 3:
Description: Calgas
Last Modified: 07/01/98 09:49 AM
Emission Current: 10 microamps
Mass Defect: 0 mmu/100u
Count Threshold: 1 counts
Multiplier Offset: 0 volts
Cal Gas: ON
Scan Time: 0.500 seconds
Segment Start Time: 1.00 minutes
Segment End Time: 1.50 minutes
Segment Low Mass: 50 m/z
Segment High Mass: 650 m/z
Ionization Mode: EI AGC
Ion Preparation Technique: NONE
EI-Auto Mode:
Maximum Ionization Time: 25000 microseconds

	Mass Range	Ion. Storage Level	Ion. Time Factor
Scan Segment 1:	10 to 99	35.0 m/z	100%
Scan Segment 2:	100 to 249	35.0 m/z	100%
Scan Segment 3:	250 to 399	35.0 m/z	100%

Scan Segment 4: 400 to 650 35.0 m/z 100%
Target TIC: 20000 counts
Prescan Ionization Time: 100 microseconds
Background Mass: 45 m/z
RF Dump Value: 650.0 m/z
No Ion Preparation.

Segment Number 4:
Description: 131
Last Modified: 11/01/00 11:59 AM
Emission Current: 10 microamps
Mass Defect: 0 mmu/100u
Count Threshold: 1 counts
Multiplier Offset: 0 volts
Cal Gas: ON
Scan Time: 0.500 seconds
Segment Start Time: 1.50 minutes
Segment End Time: 2.00 minutes
Segment Low Mass: 129 m/z
Segment High Mass: 134 m/z
Ionization Mode: EI AGC
Ion Preparation Technique: NONE
EI-Auto Mode:
Maximum Ionization Time: 25000 microseconds

	Mass Range	Ion. Storage Level	Ion. Time Factor
Scan Segment 1:	10 to 99	35.0 m/z	100%
Scan Segment 2:	100 to 249	35.0 m/z	100%
Scan Segment 3:	250 to 399	35.0 m/z	100%
Scan Segment 4:	400 to 650	35.0 m/z	100%

Target TIC: 20000 counts
Prescan Ionization Time: 100 microseconds
Background Mass: 45 m/z
RF Dump Value: 650.0 m/z
No Ion Preparation.

Segment Number 5:
Description: Leak Check
Last Modified: 11/01/00 12:00 PM
Emission Current: 10 microamps
Mass Defect: 0 mmu/100u
Count Threshold: 1 counts
Multiplier Offset: 0 volts
Cal Gas: OFF
Scan Time: 0.500 seconds
Segment Start Time: 2.00 minutes

Segment End Time: 2.50 minutes
Segment Low Mass: 50 m/z
Segment High Mass: 90 m/z
Ionization Mode: EI AGC
Ion Preparation Technique: NONE
EI-Auto Mode:
Maximum Ionization Time: 25000 microseconds

	Mass Range	Ion. Storage Level	Ion. Time Factor
Scan Segment 1:	10 to 99	35.0 m/z	100%
Scan Segment 2:	100 to 249	35.0 m/z	100%
Scan Segment 3:	250 to 399	35.0 m/z	100%
Scan Segment 4:	400 to 650	35.0 m/z	100%

Target TIC: 20000 counts
Prescan Ionization Time: 100 microseconds
Background Mass: 45 m/z
RF Dump Value: 650.0 m/z
No Ion Preparation.

Segment Number 6:
Description: Unretained Air Peak
Last Modified: 11/17/00 10:36 AM
Emission Current: 10 microamps
Mass Defect: 0 mmu/100u
Count Threshold: 1 counts
Multiplier Offset: 0 volts
Cal Gas: OFF
Scan Time: 0.500 seconds
Segment Start Time: 2.50 minutes
Segment End Time: 3.50 minutes
Segment Low Mass: 25 m/z
Segment High Mass: 35 m/z
Ionization Mode: EI Fixed
Ion Preparation Technique: NONE
EI-Fixed Mode:
Maximum Ionization Time: 25000 microseconds

	Mass Range	Ion. Storage Level	Ion. Time Factor
Scan Segment 1:	10 to 99	10.0 m/z	100%
Scan Segment 2:	100 to 249	10.0 m/z	100%
Scan Segment 3:	250 to 399	10.0 m/z	100%
Scan Segment 4:	400 to 650	10.0 m/z	100%

Ionization Time: 100 microseconds
No Ion Preparation.
****
3800 GC
****

Appendix II - Saturn GC/MS Workstation Method - IDLE.MTH

Module Address: 44

Front Valve Oven
- Oven Power: On
- Temperature: 150 C

Middle Valve Oven
- Oven Power: On
- Temperature: 62 C

Rear Valve Oven
- Oven Power: On
- Temperature: 80 C

Valve Table
- Valve 1: Sample Valve
  Initial: Off
- Valve 2: Sample Valve
  Initial: Off
- Valve 3: Sample Valve
  Initial: Off
- Valve 4: Sample Valve
  Initial: Off
- Valve 5: Internal Standard Valve
  Initial: Off

Front Injector Type 1079
- Oven Power: On
- Coolant: On
- Enable Coolant at: 250 C
- Coolant Timeout: 30.00 min

Temp (C)	Rate (C/min)	Hold (min)	Total (min)
200	0	1.00	1.00

Middle Injector Type 1079
- Oven Power: On
- Coolant: On
- Enable Coolant at: 250 C
- Coolant Timeout: 20.00 min

Temp (C)	Rate (C/min)	Hold (min)	Total (min)
200	0	1.00	1.00

Rear Injector EFC Type 3

Flow (ml/min)	Rate (ml/min/min)	Hold (min)	Total (min)
1.2	0.0	1.00	1.00

Column Oven
- Coolant: On
- Enable Coolant at: 50 C

Coolant Timeout: 20.00 min
Stabilization Time: 0.10 min

Temp (C)	Rate (C/min)	Hold (min)	Total (min)
100	0.0	1.00	1.00

Front FID Detector
Oven Power: Off
Temperature: 150 C
Electronics: Off
Time Constant: Fast

Time (min)	Range	Autozero
Initial	12	yes

Front Type 11 Detector EFC
Make up Flow: 0 ml/min
H2 Flow: 0 ml/min
Air Flow: 0 ml/min
Output Port A

Time (min)	Signal Source	Attenuation
Initial	Front	1

Output Port B

Time (min)	Signal Source	Attenuation
Initial	Front	1

Output Port C

Time (min)	Signal Source	Attenuation
Initial	Front	1

Data Acquisition
Detector Bunch Rate : 4 points (10.0 Hz)
Monitor Length: 64 bunched points (6.4 sec)
Front FID/TSD Scale: 1 Volts
Middle FID/TSD Scale: 1 Volts
Rear FID/TSD Scale: 1 Volts
**********End of Method**********

Appendix II - Saturn GC/MS Workstation Method - MTBEQUANT.MTH

****

Saturn GC/MS Workstation - Method Listing
Method: mtbequant.mth

****

MS METHOD SECTION REPORT

Last Modified:

Security Options Required:	EI
Mass Data Type:	CENTROID
Method Start Time:	-12.00 minutes
Number Of Segments:	2

Flow Sampling Segment:

Start Time:	-8.00 minutes
End Time:	-5.00 minutes
Sample Flow Rate:	50 milliliters/minute

Segment Number 1:

Description:	Filament Delay
Last Modified:	
Emission Current:	10 microamps
Mass Defect:	0 mmu/100u
Count Threshold:	1 counts
Multiplier Offset:	0 volts
Cal Gas:	OFF
Scan Time:	1.000 seconds
Segment Start Time:	0.00 minutes
Segment End Time:	0.50 minutes
Segment Low Mass:	40 m/z
Segment High Mass:	650 m/z
Ionization Mode:	NONE
Ion Preparation Technique:	NONE

No Ionization Mode
No Ion Preparation

Segment Number 2:

Description:	Data Collection
Last Modified:	
Emission Current:	30 microamps
Mass Defect:	0 mmu/100u
Count Threshold:	1 counts
Multiplier Offset:	0 volts
Cal Gas:	OFF
Scan Time:	0.620 seconds
Segment Start Time:	0.50 minutes
Segment End Time:	47.00 minutes

Segment Low Mass: 33 m/z
Segment High Mass: 350 m/z
Ionization Mode: EI AGC
Ion Preparation Technique: NONE
EI-Auto Mode:
Maximum Ionization Time: 25000 microseconds

	Mass Range	Ion. Storage Level	Ion. Time Factor
Scan Segment 1:	10 to 99	32.0 m/z	100%
Scan Segment 2:	100 to 249	32.0 m/z	100%
Scan Segment 3:	250 to 399	32.0 m/z	100%
Scan Segment 4:	400 to 650	32.0 m/z	100%

Target TIC: 20000 counts
Prescan Ionization Time: 100 microseconds
Background Mass: 33 m/z
RF Dump Value: 650.0 m/z
No Ion Preparation.

MS REPORT FORMAT METHOD

PRINT OPTIONS:

Single-Run Reports:

Sample Report:

Printed Sample Report: No
ASCII Sample Report: No

Header Configuration:

Header Description:
Sample ID Operator
Instrument ID Last Calibration
Acquisition Date Data File
Calculation Date Method
Inj. Sample Notes

Compound Report:

Printed Compound Reports: Yes
Analysis Samples: No
Verification Samples: No
Calibration Samples: No

Header Configuration:

Header Description:
Sample ID Operator
Instrument ID Last Calibration
Measurement Type Calibration Type
Acquisition Date Data File
Calculation Date Method
Sample Type
Inj. Sample Notes

Printout Scheduling: after each injection

Multi-Run Block Reports:
- Calibration Reports:
  - Printed Block Report: No
  - ASCII Block Report: No
  - Printed Curve Report: No
- Sample List Reports:
  - Print Summary Report: Yes
  - ASCII Summary Report: Yes
  - Print Control Charts: No
  - Print Control Charts: No
- ASCII Reports Column Separator:
  - Use list separator in regional settings
  - Number of copies to print: 1
  - Number of decimal digits for amounts: 3

RESULTS FORMAT:
- Results Table Format:
  - STANDARD
    - Show Ion Ratio Information: No
    - Show Compound Group Totals: No
  - Run Documentation:
    - Acquisition Segment Information: No
    - Run Log: Yes
    - Error Log: No
    - Calibration Report: No
    - Revision Log: Yes
    - Sample Notes: No
    - Method Notes: No

CHROMATOGRAM FORMAT:
- Time Scale:
  - Start Time: 0.00 minutes
  - End Time: 1440.00 minutes
  - Number of Plots: 1
  - Overlap Seconds: 3
- Amplitude Scale:
  - Autoscale (Zoom Factor = 1.00)
  - Percentage of Offset = 5%
- Plot Annotation:
  - General:
    - Acquisition Segments: Yes
  - Integration Events + Baselines: Yes
- Peak Annotation:
  - RetentionTime: Yes
  - Scan Number: No
  - Compound Name: Yes
  - Compound Number: No

Peak Types to Annotate:
- Identified: Yes
- Failed: Yes
- Missing: Yes
- TIC's: No
- Unknowns: No
- Duplicates: No

COMPOUND REPORTS:

Target Compounds:

Results:
- Type: STANDARD
- Acquisition Segment Info: Yes

Target Plots:
- Quan Ion Chromatogram: Sample Spectrum, Reference Spectrum, Raw Sample Spectrum

Unidentified Peaks:

Results:
- Type: STANDARD
- Acquisition Segment Info: Yes

Library Searched Plots:
- Quan Ion Chromatogram: Sample Spectrum, First Library Match Spectrum, Difference (Sample - 1st Match)

Plots Not Library Searched:
- Quan Ion Chromatogram

CALIBRATION BLOCK REPORT:

Block Report:
- Type: STANDARD
- Title: Calibration Block Report

Curve Report:
- Number of Curves/Page: 4
- Show Outliers on Curve: Yes
- Title: Calibration Curves Report

SAMPLE LIST REPORTS:

Include Run Types:
- Calibration: Yes
- Analysis: Yes
- Verification: Yes

Sort By:
- First Key: Compound
- Group By: First Key

Summary Report:
- Title: Summary Report
- Summarize:

Retention Time: Yes
Results (Amount): No
Area: No
Height: No

Control Charts:
Title: Control Chart
Chart: Retention Time
Control Limits: +/-2 Standard Deviations
Plot Options:
Number of Plots/Page: 4

DATA HANDLING METHOD **ADDRESS 40**

Calculations Setup
General
Measurement Type: Area
Calibration Type: External Std
Unretained Peak Time: 0.000 min
Ion Ratio Type: Absolute
Report Missing Peaks: Yes
Report Unknown Peaks: No
Normalize Results: No
Ignore Calibration Data: No
Scale Air Flow Samples: No
Chromatogram Processing
Chromatogram Processing Disabled
Results Treatment
Calibration Results
Replicates Addition Mode: Append
Replicates Addition Rule: Always add new replicates
Update Compound Table RT: Yes
Analysis Results
Calibration Range Tolerance: 20.0%
Out-of-Tolerance Action: No Action
Verification Results
Deviation Tolerance: 100.0%
Out-of-Tolerance Action: No Action

Compound Table
Entry Number: 1
Compound Name: Acetone
CAS Number: 67-64-1
Attributes: Time: 13.391 min Std: N RRT: N Active: Y
Quan Ions: 43
Scan Channels: Merged
Qualifier 1: Ion: 42 Abs Ratio: 13.7 Uncert: 20.0 L%: 0.1 H%: 33.7
Qualifier 2: Ion: 58 Abs Ratio: 6.2 Uncert: 20.0 L%: 0.1 H%: 26.2

Qualifier 3: Ion: 39 Abs Ratio: 5.2 Uncert: 20.0 L%: 0.1 H%: 25.2
Cali. Curve: Curve Fit: Linear Origin: Ignore Weight: 1/nx2
Calculations: Levels: 1 Mult: 1.000 Thresh: 0.000 Units: ppb
Level 1 Amount: 10.500
Coefficients: +0.0000e+000x^3 +0.0000e+000x^2 +8.8264e+003x +1.1369e-013
Detection: Detection Type: Normal
Integration: WI: 50.0 SS: 200 T%: 10 Area Rej: 500 Ht Rej: 100
Baseline: Baseline Type: Normal
Identification: Win: +/- 0.600 min Type: Spectrum Thrsh: 700 Int Thrsh%: 5
Ref Spectrum: 38 223; 39 520; 40 53; 41 207;
: 42 1367; 43 10000; 44 297; 52 66;
: 53 188; 54 101; 55 270; 56 173;
: 57 429; 58 622; 59 306; 61 162;

Entry Number: 2
Compound Name: MTBE
CAS Number: 1634-04-4
Attributes: Time: 17.289 min Std: N RRT: N Active: Y
Quan Ions: 73
Scan Channels: Merged
Qualifier 1: Ion: 43 Abs Ratio: 31.7 Uncert: 20.0 L%: 11.7 H%: 51.7
Qualifier 2: Ion: 41 Abs Ratio: 28.7 Uncert: 20.0 L%: 8.7 H%: 48.7
Qualifier 3: Ion: 39 Abs Ratio: 21.2 Uncert: 20.0 L%: 1.2 H%: 41.2
Cali. Curve: Curve Fit: Linear Origin: Ignore Weight: 1/nx2
Calculations: Levels: 1 Mult: 1.000 Thresh: 0.000 Units: ppb
Level 1 Amount: 5.900
Coefficients: +0.0000e+000x^3 +0.0000e+000x^2 +2.0011e+004x -9.0949e-013
Detection: Detection Type: Normal
Integration: WI: 15.0 SS: 250 T%: 10 Area Rej: 500 Ht Rej: 100
Baseline : Baseline Type: Normal
Identification: Win: +/- 0.200 min Type: Spectrum Thrsh: 700 Int Thrsh%: 5
Ref Spectrum: 37 202; 38 296; 39 2119; 40 339;
: 41 2866; 42 408; 43 3171; 44 163;
: 45 676; 50 133; 53 121; 55 694;
: 56 412; 57 1728; 73 10000; 74 472;

Entry Number: 3
Compound Name: Hexane
CAS Number: 110-54-3
Attributes: Time: 18.659 min Std: N RRT: N Active: Y
Quan Ions: 41
Scan Channels: Merged
Qualifier 1: Ion: 57 Abs Ratio: 68.1 Uncert: 20.0 L%: 48.1 H%: 88.1
Qualifier 2: Ion: 56 Abs Ratio: 66.0 Uncert: 20.0 L%: 46.0 H%: 86.0
Qualifier 3: Ion: 39 Abs Ratio: 54.2 Uncert: 20.0 L%: 34.2 H%: 74.2

Cali. Curve: Curve Fit: Linear Origin: Ignore Weight: 1/nx2
Calculations: Levels: 1 Mult: 1.000 Thresh: 0.000 Units: ppb
Level 1 Amount: 7.400
Coefficients: +0.0000e+000x^3 +0.0000e+000x^2 +6.9833e+003x -1.1369e-013
Detection: Detection Type: Normal
Integration: WI: 10.0 SS: 100 T%: 10 Area Rej: 500 Ht Rej: 100
Baseline: Baseline Type: Normal
Identification: Win: +/- 0.200 min Type: Spectrum Thrsh: 700 Int Thrsh%: 5
Ref Spectrum: 37 356; 38 609; 39 5419; 40 755;
: 41 10000; 42 1847; 43 2891; 50 240;
: 53 248; 55 977; 56 6601; 57 6814;
: 58 349; 71 530; 85 627; 86 253;

Entry Number: 4
Compound Name: ETBE
CAS Number: 637-92-3
Attributes: Time: 19.798 min Std: N RRT: N Active: Y
Quan Ions: 59
Scan Channels: Merged
Qualifier 1: Ion: 87 Abs Ratio 54.1 Uncert: 20.0 L%: 34.1 H%: 74.1
Qualifier 2: Ion: 41 Abs Ratio: 24.8 Uncert: 20.0 L%: 4.8 H%: 44.8
Qualifier 3: Ion: 57 Abs Ratio: 21.5 Uncert: 20.0 L%: 1.5 H%: 41.5
Cali. Curve: Curve Fit: Linear Origin: Ignore Weight: 1/nx2
Calculations: Levels: 1 Mult: 1.000 Thresh: 0.000 Units: ppb
Level 1 Amount: 5.900
Coefficients: +0.0000e+000x^3 +0.0000e+000x^2 +1.6459e+004x -4.5475e-013
Detection: Detection Type: Normal
Integration: WI: 15.0 SS: 200 T%: 10 Area Rej: 500 Ht Rej: 100
Baseline: Baseline Type: Normal
Identification: Win: +/- 0.200 min Type: Spectrum Thrsh: 700 Int Thrsh%: 5
Ref Spectrum : 38 235; 39 1784; 40 207; 41 2475;
: 42 357; 43 1165; 45 187; 55 279;
: 56 514; 57 2145; 58 208; 59 10000;
: 60 365; 86 251; 87 5407; 88 385;

Entry Number: 5
Compound Name: tert- Butyl formate
CAS Number: 762-75-4
Attributes: Time: 20.614 min Std: N RRT: N Active: Y
Quan Ions: 59
Scan Channels: Merged
Qualifier 1: Ion: 41 Abs Ratio: 82.4 Uncert: 20.0 L%: 62.4 H%: 102.4
Qualifier 2: Ion: 57 Abs Ratio: 68.8 Uncert: 20.0 L%: 48.8 H%: 88.8
Qualifier 3: Ion: 39 Abs Ratio: 66.4 Uncert: 20.0 L%: 46.4 H%: 86.4
Cali. Curve: Curve Fit: Linear Origin: Ignore Weight: 1/nx2

Calculations: Levels: 1 Mult: 1.000 Thresh: 0.000 Units: ppb
Level 1 Amount: 7.000
Coefficients: +0.0000e+000x^3 +0.0000e+000x^2 +7.3839e+002x +0.0000e+000
Detection: Detection Type: Normal
Integration: WI: 15.0 SS: 200 T%: 10 Area Rej: 500 Ht Rej: 100
Baseline: Baseline Type: Normal
Identification: Win: +/- 0.200 min Type: Spectrum Thrsh: 700 Int Thrsh%: 5
Ref Spectrum: 37 764; 38 862; 39 6635; 40 1104;
: 41 8240; 42 557; 43 1863; 44 465;
: 45 322; 50 362; 55 1150; 56 3513;
: 57 6883; 58 540; 59 10000; 60 339;

Entry Number: 6
Compound Name: Benzene
CAS Number: 71-43-2
Attributes: Time: 22.324 min Std: N RRT: N Active: Y
Quan Ions: 78
Scan Channels: Merged
Qualifier 1: Ion: 77 Abs Ratio: 32.6 Uncert: 20.0 L%: 12.6 H%: 52.6
Qualifier 2: Ion: 50 Abs Ratio: 24.1 Uncert: 20.0 L%: 4.1 H%: 44.1
Qualifier 3: Ion: 51 Abs Ratio: 22.3 Uncert: 20.0 L%: 2.3 H%: 42.3
Cali. Curve: Curve Fit: Linear Origin: Ignore Weight: 1/nx2
Calculations: Levels: 1 Mult: 1.000 Thresh: 0.000 Units: ppb
Level 1 Amount: 6.000
Coefficients: +0.0000e+000x^3 +0.0000e+000x^2 +1.1867e+004x +2.2737e-013
Detection: Detection Type: Normal
Integration: WI: 15.0 SS: 200 T%: 10 Area Rej: 500 Ht Rej: 100
Baseline: Baseline Type: Normal
Identification: Win: +/- 0.200 min Type: Spectrum Thrsh: 700 Int Thrsh%: 5
Ref Spectrum: 37 710; 38 656; 39 1038; 49 486;
: 50 2412; 51 2232; 52 1738; 62 137;
: 63 531; 73 167; 74 398; 75 162;
: 76 733; 77 3255; 78 10000; 79 672;

Entry Number: 7
Compound Name: tert-amyl methyl ether
CAS Number: 994-05-8
Attributes: Time: 22.774 min Std: N RRT: N Active: Y
Quan Ions: 73
Scan Channels: Merged
Qualifier 1: Ion: 43 Abs Ratio: 42.4 Uncert: 20.0 L%: 22.4 H%: 62.4
Qualifier 2: Ion: 55 Abs Ratio: 37.0 Uncert: 20.0 L%: 17.0 H%: 57.0
Qualifier 3: Ion: 87 Abs Ratio: 27.5 Uncert: 20.0 L%: 7.5 H%: 47.5
Cali. Curve: Curve Fit: Linear Origin: Ignore Weight: 1/nx2
Calculations: Levels: 1 Mult: 1.000 Thresh: 0.000 Units: ppb

Level 1 Amount: 4.400
Coefficients: +0.0000e+000x^3 +0.0000e+000x^2 +1.2201e+004x -4.5475e-013
Detection: Detection Type: Normal
Integration: WI: 15.0 SS: 100 T%: 10 Area Rej: 500 Ht Rej: 100
Baseline: Baseline Type: Normal
Identification: Win: +/- 0.200 min Type: Spectrum Thrsh: 700 Int Thrsh%: 5
Ref Spectrum : 38 279; 39 1899; 40 322; 41 2130;
: 42 699; 43 4239; 44 246; 45 1020;
: 53 327; 55 3698; 57 334; 70 428;
: 71 1213; 73 10000; 74 465; 87 2752;

****
3800 GC
****
Module Address: 44

Front Valve Oven
Oven Power: On
Temperature: 150 C
Middle Valve Oven
Oven Power: On
Temperature: 62 C
Rear Valve Oven
Oven Power: On
Temperature: 80 C
Valve Table
Valve 1: Sample Valve
Initial: Off
0.01 min: On
2.00 min: On
5.00 min: Off
8.00 min: Off
11.00 min: Off
12.00 min: Off
14.00 min: Off
Valve 2: Sample Valve
Initial: Off
0.01 min: Off
2.00 min: On
5.00 min: On
8.00 min: Off
11.00 min: Off
12.00 min: Off
14.00 min: Off
Valve 3: Sample Valve

Initial: Off
0.01 min: Off
2.00 min: Off
5.00 min: Off
8.00 min: Off
11.00 min: Off
12.00 min: On
14.00 min: Off

Valve 4: Sample Valve
Initial: Off
0.01 min: Off
2.00 min: Off
5.00 min: Off
8.00 min: Off
11.00 min: On
12.00 min: Off
14.00 min: Off

Valve 5: Internal Standard Valve
Initial: Off
0.01 min: Off
2.00 min: Off
5.00 min: Off
8.00 min: Off
11.00 min: Off
12.00 min: Off
14.00 min: Off

Front Injector Type 1079
Oven Power: On
Coolant: On
Enable Coolant at: 250 C
Coolant Timeout: 30.00 min

Temp (C)	Rate (C/min)	Hold (min)	Total (min)
100	0	8.00	8.00
250	200	50.25	59.00

Middle Injector Type 1079
Oven Power: On
Coolant: On
Enable Coolant at: 250 C
Coolant Timeout: 20.00 min

Temp (C)	Rate (C/min)	Hold (min)	Total (min)
200	0	4.00	4.00
-30	200	5.85	11.00
250	200	46.60	59.00

Appendix II - Saturn GC/MS Workstation Method - MTBEQUANT.MTH

Rear Injector EFC Type 3

Flow (ml/min)	Rate (ml/min/min)	Hold (min)	Total (min)
1.2	0.0	51.00	51.00
2.0	2.0	7.60	59.00

Column Oven

Coolant: On
Enable Coolant at: 50 C
Coolant Timeout: 20.00 min
Stabilization Time: 0.10 min

Temp (C)	Rate (C/min)	Hold (min)	Total (min)
100	0.0	7.00	7.00
-10	100.0	4.40	12.50
200	5.0	4.50	59.00

Front FID Detector

Oven Power: Off
Temperature: 60 C
Electronics: Off
Time Constant: Fast

Time (min)	Range	Autozero
Initial	12	yes

Front Type 11 Detector EFC

Make up Flow: 0 ml/min
H2 Flow: 0 ml/min
Air Flow: 0 ml/min

Output Port A

Time (min)	Signal Source	Attenuation
Initial	Front	1

Output Port B

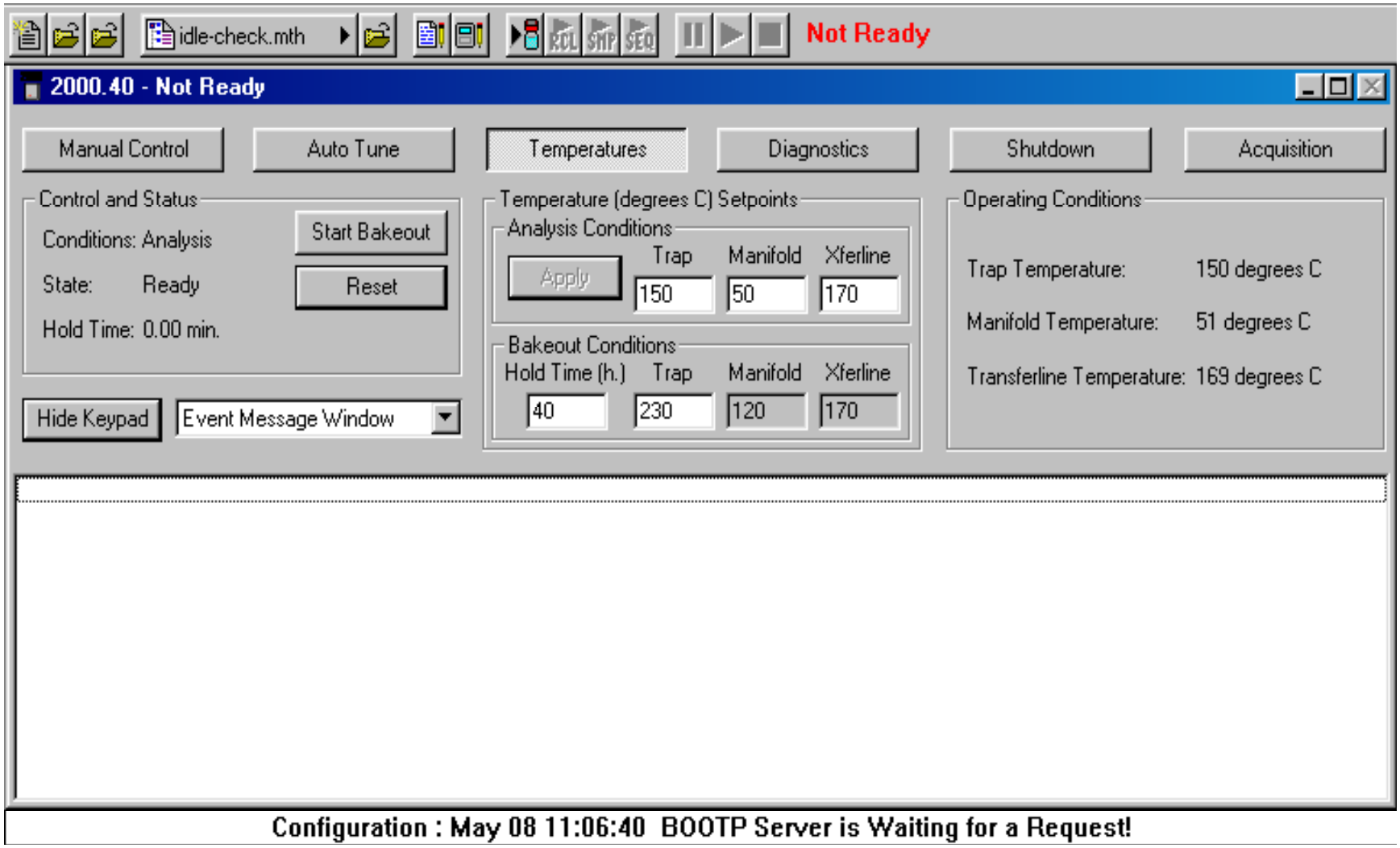
Time (min)	Signal Source	Attenuation
Initial	Front	1

Output Port C

Time (min)	Signal Source	Attenuation
Initial	Front	1

*******End of Method**********

Additional Temperature Settings



Sample List

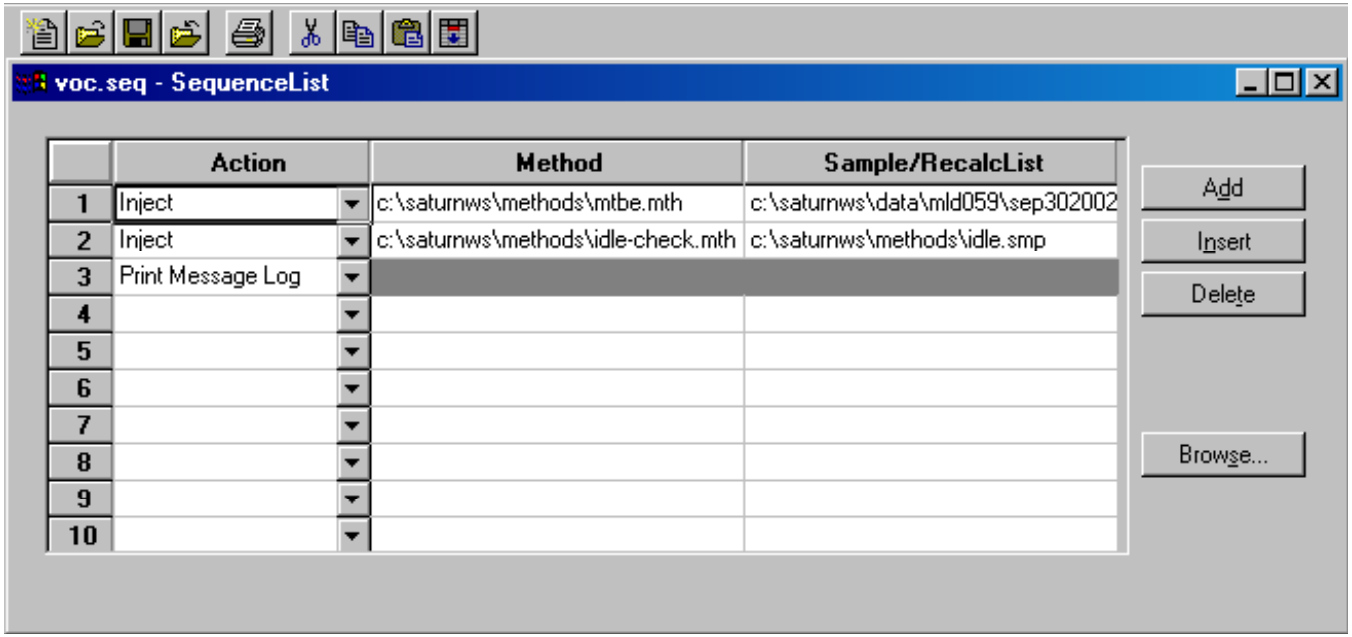
093002.smp - Generic SampleList

	Sample Name	Sample Type	Cal. level	Inj.	Injection Notes	AutoLink	Amount Std (IS, N% only)	Unid Peak Factor	Multiplier	Divisor	MultiChannel MultiStandard
1		Autolink				ssvauto.exe					
2	LN2	Analysis		1	none	ssvauto.exe	1	0	1	1	none
3	AAL053319	Analysis		1	none	ssvauto.exe	2	0	1	1	none
4	CC109953	Analysis		1	none	ssvauto.exe	3	0	1	1	none
5	LN2	Analysis		1	none	ssvauto.exe	1	0	1	1	none
6	TX004748 AZ	Analysis		1	none	ssvauto.exe	4	0	1	1	none
7	TX004699 FV	Analysis		1	none	ssvauto.exe	5	0	1	1	none
8	TX004751 LB	Analysis		1	none	ssvauto.exe	6	0	1	1	none
9	TX004702 FF	Analysis		1	none	ssvauto.exe	7	0	1	1	none
10	TX004726 RU-REG	Analysis		1	none	ssvauto.exe	8	0	1	1	none
11	TX004729 RU-COL	Analysis		1	none	ssvauto.exe	9	0	1	1	none
12	TX004701 CX	Analysis		1	none	ssvauto.exe	10	0	1	1	none
13	TX004704 BB	Analysis		1	none	ssvauto.exe	11	0	1	1	none
14	TX004698 CR	Analysis		1	none	ssvauto.exe	12	0	1	1	none
15	TX004705 EC	Analysis		1	none	ssvauto.exe	13	0	1	1	none
16	TX004748A AZ	Analysis		1	none	ssvauto.exe	4	0	1	1	none
17	CC109953	Analysis		1	none	ssvauto.exe	3	0	1	1	none
18	AAL053319	Analysis		1	none	ssvauto.exe	2	0	1	1	none
19	LN2	Analysis		1	none	ssvauto.exe	1	0	1	1	none
20											

Add
Insert
Delete
Fill Down
Add Lines...
Defaults...
Data Files...
RecalcList...

Appendix II - Saturn GC/MS Work Station Method – Screen Shots

Sequence List



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Appendix III: Star GC Workstation

A Varian Star GC Workstation includes an Intel compatible PC, an Ethernet network adapter, Microsoft 9.X, NT 4.0, or newer, operating system, and Varian Star Chromatography Workstation software, Version 5.52 or newer. The GC Workstation automates control of the integrated Varian/Lotus Cryogenic/Adsorbent Concentration system. This automation covers:

- Concentration of the sample;
- Introduction of the concentrated sample onto the GC column;
- GC carrier gas flow;
- Set points for the temperature of the concentrator heated zones 1 through 6;
- Starting of the associated HP 6890/5973 GC/MSD system.

For a more detailed discussion of the Star Chromatography Workstation software, including setting up methods, sequences, and sample lists, refer to the following manuals on CD-ROM:

- “Varian Star Chromatography Workstation”, Version 5.51 CD-ROM
- “Varian Saturn GC/MS Workstation – System Software”, Version 5.52 CD-ROM

Additional resources by Randall Bramston-Cook of Lotus Consulting are:

- “Ultra Trace Hydrocarbon System Operator’s Manual”
- “Stream Selector Valve Control Software for Varian Workstation Operator’s Manual”
- "Varian GC Star Workstation Manual"

The instrument setpoints are stored on the Workstation as methods. Method MLD050B.MTH is used for normal operation. Sections that are not used in a particular method are shown in lighter type.

A copy of the Varian Star Workstation acquisition method is listed on the following pages. Sections that are not used in a particular method are shown in lighter type. Screen shots of the Sample List, and the Sequence List are shown on pages 86 and 87 in Appendix II, under the Varian Saturn GC/MS Workstation. The GC and GC/MS Workstations share a common view of these items.

Appendix III - Star GC Work Station Method – MLD050B.MTH

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Star GC Workstation - Method Listing
Method: mld050b.mth

****

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Notes

****

****

3800 GC

****

Module Address: 44

Middle Valve Oven
- Oven Power: On
- Temperature: 120 C

Rear Valve Oven
- Oven Power: On
- Temperature: 50 C

Valve Table

Valve 1:		Sample Valve
	Initial:	Off
	0.01 min:	On
	2.00 min:	On
	5.00 min:	Off
	9.00 min:	Off
	12.00 min:	Off
	17.00 min:	Off
Valve 2:		Sample Preconcentration Trap Valve
	Initial:	SPT Desorb
	0.01 min:	SPT Desorb
	2.00 min:	SPT Trap
	5.00 min:	SPT Trap
	9.00 min:	SPT Desorb
	12.00 min:	SPT Desorb
	17.00 min:	SPT Desorb
Valve 3:		Sample Preconcentration Trap Valve
	Initial:	SPT Desorb
	0.01 min:	SPT Desorb
	2.00 min:	SPT Desorb
	5.00 min:	SPT Desorb
	9.00 min:	SPT Desorb
	12.00 min:	SPT Trap
	17.00 min:	SPT Desorb
Valve 4:		Series Bypass Valve
	Initial:	Series

0.01 min: Series
2.00 min: Series
5.00 min: Series
9.00 min: Series
12.00 min: Series
17.00 min: Series
Valve 5: Event A Valve
Initial: Off
0.01 min: Off
2.00 min: Off
5.00 min: Off
9.00 min: Off
12.00 min: On
17.00 min: Off
Valve 6: Event B Valve
Initial: Off
0.01 min: Off
2.00 min: Off
5.00 min: Off
9.00 min: Off
12.00 min: Off
17.00 min: Off
Valve 7: Event C Valve
Initial: Off
0.01 min: Off
2.00 min: Off
5.00 min: Off
9.00 min: Off
12.00 min: Off
17.00 min: Off

Front Injector Type 1079
Oven Power: On
Coolant: On
Enable Coolant at: 300 C
Coolant Timeout: 20.00 min

Temp (C)	Rate (C/min)	Hold (min)	Total (min)
115	0	9.00	9.00
325	200	34.95	45.00

Middle Injector Type 1079
Oven Power: On
Coolant: On
Enable Coolant at: 300 C
Coolant Timeout: 20.00 min

Temp (C)	Rate (C/min)	Hold (min)	Total (min)
200	0	5.00	5.00
-30	200	5.85	12.00
325	200	31.22	44.99

Rear Injector Type 1041

Oven Power:	On
Temperature:	150 C

Rear Injector EFC Type 3

Flow (ml/min)	Rate (ml/min/min)	Hold (min)	Total (min)
2.0	0.0	45.00	45.00

Column Oven

Coolant:	Off
Enable Coolant at:	50 C
Coolant Timeout:	20.00 min
Stabilization Time:	0.50 min

Temp (C)	Rate (C/min)	Hold (min)	Total (min)
50	0.0	55.00	55.00

Front FID Detector

Oven Power:	Off
Temperature:	50 C
Electronics:	On
Time Constant:	Fast

Time (min)	Range	Autozero
Initial	12	no

Output Port A

Time (min)	Signal Source	Attenuation
Initial	Front	1

Output Port B

Time (min)	Signal Source	Attenuation
Initial	Front	1

Output Port C

Time (min)	Signal Source	Attenuation
Initial	Front	1

Data Acquisition

Detector Bunch Rate :	128 points (0.3 Hz)
Monitor Length :	16 bunched points (51.2 sec)
Front FID/TSD Scale:	1 Volts

Middle FID/TSD Scale: 1 Volts
Rear FID/TSD Scale: 1 Volts

Integration Parameters Address 44 Channel Front
Subtract Blank Baseline: No
Initial S/N Ratio: 5
Initial Peak Width: 4 sec
Initial Tangent Height %: 10%
Monitor Noise: Once at start of method
Measurement Type: Peak Area
Initial Peak Reject Value: 1000 counts
Report Unidentified Peaks: No
Report Missing Peaks: No

Calibration Setup Address 44 Channel Front
Calculation Type: % (No Calibration)
Number of Calibration Levels: 1
Curve Origin: Force
Curve Fit: Linear
Weighted Regression: (None)
Replicate Treatment: Average Calibration Replicates
Averaging Weight: 50% (applied to new replicates)
Replicate Tolerance: Add replicates within tolerance of 0.5%
Out-of-Tolerance Action: No Action
Calibration Range Tolerance : 10.0%
Out-of-Tolerance Action: No Action

Verification Setup Address 44 Channel Front
Deviation Tolerance: 100.0%
Out-of-Tolerance Action: No Action

Peak Table Address 44 Channel Front
Reference Peaks Time Windows: Width: 0.10 min. Retention Time 2.0%
Other Peaks Time Windows: Width: 0.10 min. Retention Time 2.0%
Peak Table Empty

Time Events Table Address 44 Channel Front
Time Events Table Empty

Report Format: Module 3800 Address 44 Channel Front
Title:
Print Chromatogram: No
Print Results: No
Convert Results to ASCII?: Off
Calibration Block Reports
Print Report: No
Convert Report to ASCII? : Off
Print Copies: 1

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Appendix IV: Agilent GC/MS ChemStation

A Agilent GC/MS Chemstation includes an Intel compatible PC, an Ethernet network adapter, a GPIB interface card, Microsoft 9.X, NT 4.0, or newer operating system, and Agilent Analytical MSD Productivity ChemStation Software, Version B.03.00, or newer. The Agilent ChemStation automates control of the Agilent Model 6890 Gas Chromatograph and it's associated Model 5973 Mass Selective Detector (MSD). This automation includes:

- Set points for the temperature of the GC column oven and the GC to MSD transfer line;
- All operating and data acquisition parameters of the MSD.

This software is also used for the analysis and reporting of the acquired MS data. For a more detailed discussion of the ChemStation software, including setting up methods, sequences, and sample lists, and data analysis, refer to the manuals, on CD-ROM:

- “HP 5973 MSD Reference Collection”, Revision C.00.00, by Agilent

The instrument setpoints are stored on the Chemstation as methods. Method MLD050M.M is used for normal operation. Method MLD050M.M also includes data handling and reporting sections.

A copy of the Agilent Chemstation acquisition method, including sections for data handling and reporting, is listed on the following pages. Sections that are not used in a particular method are shown in lighter type. An example sequence list screen is also shown.

Appendix IV - Agilent ChemStation Method - MLD050M.M

TOPLEVEL PARAMETERS

Method Information For: C:\HPCHEM\3\METHODS\MLD059.M
Method Sections To Run:

( ) Save Copy of Method With Data
( ) Pre-Run Cmd/Macro =
(X) Data Acquisition
(X) Data Analysis
( ) Post-Run Cmd/Macro =

Method Comments:
This is a method for the analysis of ambient air for toxic analytes.

END OF TOPLEVEL PARAMETERS

INSTRUMENT CONTROL PARAMETERS

Sample Inlet: GC
Injection Source: External Device
Injection Location: Front
Mass Spectrometer: Enabled

==========

HP6890 GC METHOD

==========

OVEN
Initial temp: -10 'C (On)
Initial time: 2.00 min
Ramps:

#	Rate	Final temp	Final time
1	5.00	160	1.00
2	0.0(Off)		

Post temp: 0 'C
Post time: 0.00 min
Run time: 37.00 min
Maximum temp: 260 'C
Equilibration time: 0.50 min
CRYO (N2)
Cryo: On
Cryo fault: On
Cryo timeout: 60.00 min (On)
Quick cryo cool: On
Ambient temp: 55 'C

FRONT INLET (HP PTV)
Mode: Split
Initial temp: 50 'C (On)
Initial time: 0.00 min
Ramps:

#	Rate	Final temp	Final time
1	0.0(Off)		

Cryo: Off
Cryo use temp: 25 'C
Cryo Timeout:: 30.00 min (On)
Cryo Fault: On
Pressure: 1.71 psi (On)
Split ratio: 50:1
Split flow: 98.4 mL/min

BACK INLET (SPLIT/SPLITLESS)
Mode: Split
Initial temp: 50 'C (Off)
Pressure: 0.00 psi (Off)
Total flow: 45.0 mL/min
Gas saver: Off
Gas type: Helium

Total flow: 103.4 mL/min
Gas saver: Off
Gas type: Helium

COLUMN 1
Capillary Column
Model Number: J & W DB-VRX
60m x 0.25 mm i.d. and 1.4 um thick
Max temperature: 260 'C
Nominal length: 30.0 m
Nominal film thickness: 1.80 um
Mode: constant pressure
Pressure: 1.71 psi
Nominal initial flow: 2.0 mL/min
Average velocity: 49 cm/sec
Inlet: Front Inlet
Outlet: MSD
Outlet pressure: vacuum

COLUMN 2
(not installed)

FRONT DETECTOR (NO DET)
SIGNAL 1
Data rate: 20 Hz
Type: test plot
Save Data: Off
Zero: 0.0 (Off)
Range: 0
Fast Peaks: Off
Attenuation: 0

BACK DETECTOR (NO DET)
SIGNAL 2
Data rate: 20 Hz
Type: test plot
Save Data: Off
Zero: 0.0 (Off)
Range: 0
Fast Peaks: Off
Attenuation: 0

COLUMN COMP 1
(No Detectors Installed)

COLUMN COMP 2
(No Detectors Installed)

THERMAL AUX 2
Use: MSD Transfer Line Heater
Description: MSD
Initial temp: 260 'C (On)
Initial time: 0.00 min

#	Rate	Final temp	Final time
1	0.0(Off)		

POST RUN
Post Time: 0.00 min

TIME TABLE

Time	Specifier	Parameter & Setpoint

7673 Injector
Front Injector:
No parameters specified
Back Injector:
Sample Washes 0

Sample Pumps	0
Injection Volume	1.0 microliters
Syringe Size	10.0 microliters
PostInj Solvent A Washes	0
PostInj Solvent B Washes	0
Viscosity Delay	0 seconds
Plunger Speed	Fast
PreInjection Dwell	0.00 minutes
PostInjection Dwell	0.00 minutes

MS ACQUISITION PARAMETERS

General Information

Tune File:	ATUNE.U		
Acquistion Mode:	Scan		

MS Information

Solvent Delay:	5.50 min		
EM Absolute:	False		
EM Offset:	106		
Resulting EM Voltage:	2294.1		

[Scan Parameters]

Low Mass:	35		
High Mass:	350		
Threshold:	150		
Sample #:	2	A/D Samples	4

[MSZones]

MS Quad:	150 C	maximum	200 C
MS Source:	230 C	maximum	250 C

Timed Events

[Timed MS Detector Entries]

Time (min)	State (MS on/off)
38.00	Off

END OF MS ACQUISITION PARAMETERS

END OF INSTRUMENT CONTROL PARAMETERS

DATA ANALYSIS PARAMETERS

Method Name: C:\HPCHEM\3\METHODS\MLD050M.M

Percent Report Settings

Sort By:	Signal
Output Destination	
Screen:	No
Printer:	Yes
File:	No
Integration Events:	AutoIntegrate
Generate Report During Run Method:	Yes

Signal Correlation Window:	0.020
Qualitative Report Settings	
Peak Location of Unknown:	Apex
Library to Search	Minimum Quality
C:\DATABASE\NIST98.L	25
Integration Events:	AutoIntegrate
Report Type:	Summary
Output Destination	
Screen:	No
Printer:	Yes
File:	No
Generate Report During Run Method:	Yes
Quantitative Report Settings	
Report Type:	Summary
Output Destination	
Screen:	Yes
Printer:	No
File:	No
Generate Report During Run Method:	No
Calibration Last Updated:	
Reference Window:	2.00 Minutes
Non-Reference Window:	1.00 Minutes
Correlation Window:	0.10 minutes
Default Multiplier:	1.00
Default Sample Concentration:	0.00

Compound Information

1) Ethanol ( )

Ret. Time 10.29 min., Extract & Integrate from 10.09 to 10.49 min.

Signal		Rel Resp	Pct. Unc.(abs)	Integration
Tgt	45.00			*** AUTO ***
Q1	46.00	40.00	20.0	*** AUTO ***
Q2	43.00	10.00	10.0	*** AUTO ***

Lvl	ID	Conc (ppb)	Response
1		26.400	1444365

Qualifier Peak Analysis ON

Curve Fit: Linear

2) Acetone ( )

Ret. Time 12.20 min., Extract & Integrate from 12.00 to 12.40 min.

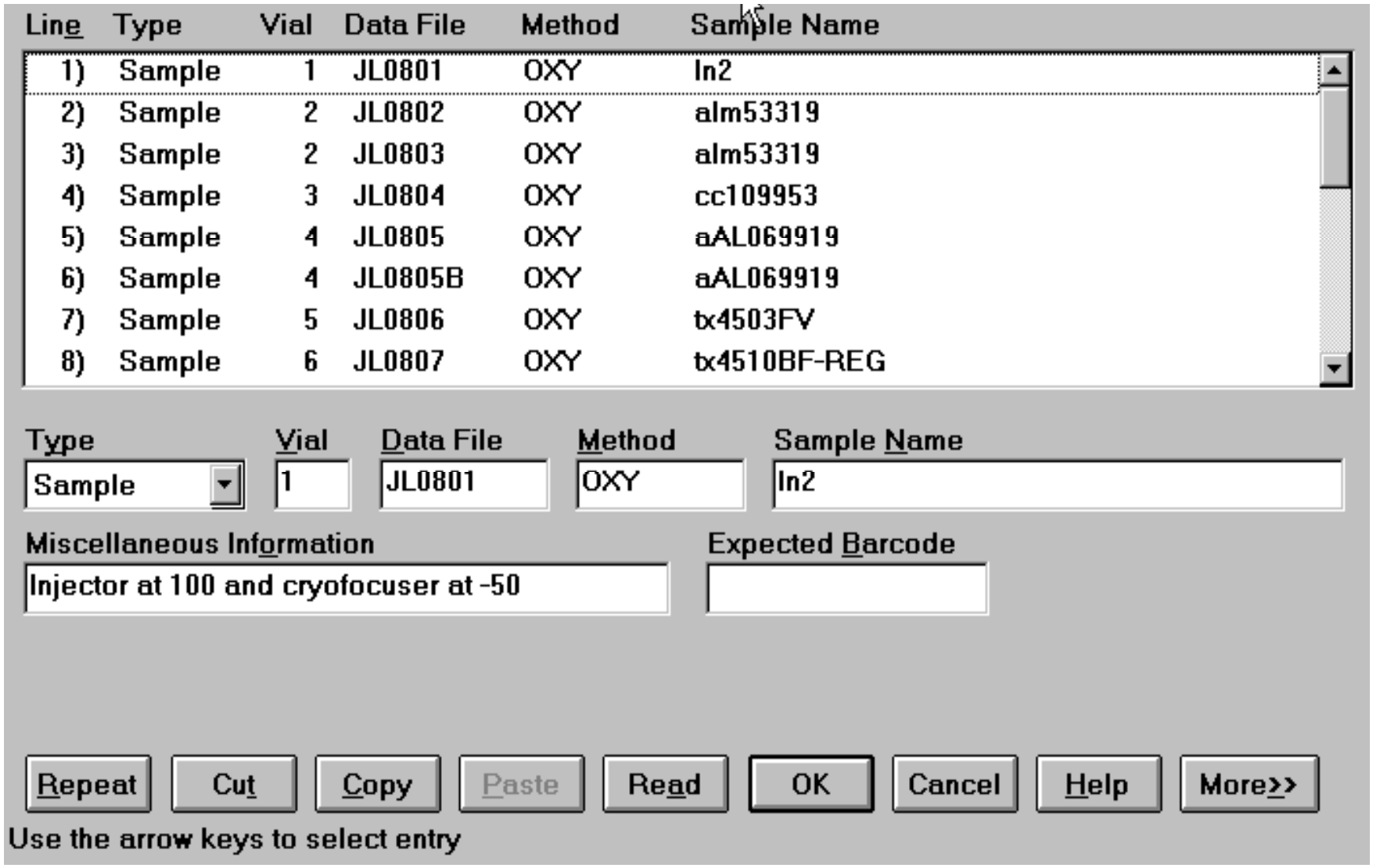
Signal		Rel Resp.	Pct. Unc.(abs)	Integration
Tgt	43.00			*** AUTO ***
Q1	58.00	40.00	20.0	*** AUTO ***
Q2	44.00	5.00	20.0	*** AUTO ***

	Lvl ID	Conc (ppb)	Response		
	1	10.500	5644533		
	Qualifier Peak Analysis		ON		
	Curve Fit:		Linear		
3)	MTBE			( )	
	Ret. Time	15.88 min.,	Extract & Integrate from	15.68	to 16.08 min.
	Signal		Rel Resp.	Pct. Unc.(abs)	Integration
	Tgt	73.00			*** AUTO ***
	Q1	57.00	20.00	20.0	*** AUTO ***
	Q2	74.00	4.00	20.0	*** AUTO ***
	Q3	87.00	0.50	20.0	*** AUTO ***
	Lvl ID	Conc (ppb)	Response		
	1	5.900	7395876		
	Qualifier Peak Analysis		ON		
	Curve Fit:		Linear		
4)	Hexane			( )	
	Ret. Time	17.19 min.,	Extract & Integrate from	16.99	to 17.39 min.
	Signal		Rel Resp.	Pct. Unc.(abs)	Integration
	Tgt	57.00			*** AUTO ***
	Q1	86.00	22.00	20.0	*** AUTO ***
	Q2	56.00	55.00	20.0	*** AUTO ***
	Q3	43.00	55.00	20.0	*** AUTO ***
	Lvl ID	Conc (ppb)	Response		
	1	7.400	4034786		
	Qualifier Peak Analysis		ON		
	Curve Fit:		Linear		
5)	ETBE			( )	
	Ret. Time	18.33 min.,	Extract & Integrate from	18.13	to 18.53 min.
	Signal		Rel Resp.	Pct. Unc.(abs)	Integration
	Tgt	59.00			*** AUTO ***
	Q1	87.00	49.00	20.0	*** AUTO ***
	Q2	57.00	32.00	20.0	*** AUTO ***
	Q3	88.00	3.00	20.0	*** AUTO ***
	Lvl ID	Conc (ppb)	Response		
	1	5.900	7421246		
	Qualifier Peak Analysis		ON		
	Curve Fit:		Linear		
6)	TBF			( )	
	Ret. Time	19.07 min.,	Extract & Integrate from	18.87	to 19.27 min.
	Signal		Rel Resp.	Pct. Unc.(abs)	Integration
	Tgt	59.00			*** AUTO ***
	Q1	57.00	81.00	20.0	*** AUTO ***
	Q2	87.00	16.00	20.0	*** AUTO ***
	Q3	72.00	1.50	20.0	*** AUTO ***

	Lvl	ID	Conc (ppb)	Response	
	1		5.000	516922	
	Qualifier Peak Analysis			ON	
	Curve Fit:			Linear	
7)	Benzene			( )	
	Ret. Time	20.65 min.,	Extract & Integrate from	20.45 to	20.85 min.
	Signal		Rel Resp.	Pct. Unc.(abs)	Integration
	Tgt	78.00			*** AUTO ***
	Q1	77.00	23.00	20.0	*** AUTO ***
	Q2	51.00	15.00	20.0	*** AUTO ***
	Lvl	ID	Conc (ppb)	Response	
	1		6.000	9475330	
	Qualifier Peak Analysis			ON	
	Curve Fit:			Linear	
8)	TAME			( )	
	Ret. Time	21.17 min.,	Extract & Integrate from	20.97 to	21.37 min.
	Signal		Rel Resp.	Pct. Unc.(abs)	Integration
	Tgt	73.00			*** AUTO ***
	Q1	87.00	27.00	20.0	*** AUTO ***
	Q2	55.00	36.00	20.0	*** AUTO ***
	Q3	71.00	12.00	20.0	*** AUTO ***
	Lvl	ID	Conc (ppb)	Response	
	1		4.400	5372618	
	Qualifier Peak Analysis			ON	
	Curve Fit:			Linear	

END OF DATA ANALYSIS PARAMETERS

Sample List


Line Type Vial Data File Method Sample Name
1) Sample 1 JL0801 OXY In2
2) Sample 2 JL0802 OXY alm53319
3) Sample 2 JL0803 OXY alm53319
4) Sample 3 JL0804 OXY cc109953
5) Sample 4 JL0805 OXY aAL069919
6) Sample 4 JL0805B OXY aAL069919
7) Sample 5 JL0806 OXY tx4503FV
8) Sample 6 JL0807 OXY tx4510BF-REG
Type
Sample
Vial
1
Data File
JL0801
Method
OXY
Sample Name
In2
Miscellaneous Information
Injector at 100 and cryofocuser at -50
Expected Barcode
Repeat
Cut
Copy
Paste
Read
OK
Cancel
Help
More>>
Use the arrow keys to select entry

Appendix V: Additional Setpoints

He Carrier Gas:

Set Rear Type 3 Electronic Flow Controller to 1.2 cm^3/minute

N_2 Purge Gas:

Set digital gauge on Flow Controller to 50.0 (~ cm^3/minute)

He Purge Gas:

Set digital gauge on Flow Controller to 20.0 (~ cm^3/minute)

Mass Flow Controller (MFC):

Set sampling flow rate to 50 cm^3/minute

Set .....50.0% of full scale
Read .....51.7% of full scale

Note: 100 cm^3/minute equals 100% full scale

Required Regulator Pressures:

He - Carrier Gas and Purge Gas .....80 psi

N_2 - Purge Gas and Nafion™ Dryer Gas.....80 psi

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Appendix VI - Procedure for Running Varian Saturn System

1. DAILY CHECK OF THE SYSTEM

In Manual Control, activate the DailyChecks method (C:\Saturn WS\Service\-Method\DailyChecks.mth).

A) Air/H2O Check (method segment 1):

Range:	10-45
Scan (Ionization) Mode:	EI-fixed
Ionization time:	100 µsec

Turn on the Trap and evaluate the Air/Water Spectrum.

Ion Count (TIC):	< 1000
100% value:	150 - 200
Ion 18 (H2O) / Ion 28 (N2):	= 2:1 or 1:2
Ion 32 (O2):	= 25% Ion 28 (N2)
Ion 19/Ion 20	= < 20%

B) High Mass Check (method segment 2)

Range:	50-650
Scan Mode:	EI Auto

Turn off the filament and check for the presence of High Mass Noise. It should be a relatively flat baseline ⇒ no HMN.

Background (TIC)	< 5000 with filament on.
Ionization time	= 25000

C) Cal Gas Check (method segment 3):

Turn on the FC-43 (perfluorotributylamine) Cal gas by clicking on the Cal Gas Symbol.
Verify the presence of ions: 69, 131, 264, 414, 464, 502, 614.

D) Ion131/ Isotope 132 Check (method segment 4):

AGC Target.

Valley/Isotope ratio:	<=25%

If necessary, adjust Axial Modulation (3.5 – 4.0 V for VOC analysis) and reevaluate.

E) Adjust Cal Gas (From the “Adjustment” tab):

Adjust only when needed (i.e.: when EM setting is changed or major maintenance is performed).
Bar graph should be close to the middle section (one bar to the right of “OK”).
Use the needle valve to increase or decrease the Cal Gas flow.
Click “Done” when finished.

Criteria: 500 – 750 usec

F) Adjust RF Tuning:

Adjust only when needed (i.e., approximately every 6 months).
Click ON Adjustment RF tune.
Adjust RF potentiometer with a flat blade screwdriver to obtain the lowest High reading (i.e., a near straight-line slope on the graph).

Average criteria:	300-500 (<1000).
Highest criteria:	500-900 (<1500).

Click “Done” when finished.

2. AUTOTUNE

A) Air/Water:

Perform this check Daily.
Should show “No Problem Found” to be acceptable.
Use same criteria as in manual control.

B) Mass Calibration:

Perform this check Daily.

Slope Optimal:	= 6.25 (should be < 6.3)
Std Dev Optimal:	= 0.05 (should be < 0.15)

C) Electron Multiplier:

Perform this check only if it’s necessary (i.e., approximately every 2 weeks).

Integrator Zero set:

Setting optimal:	= 128 (Range: 110 – 160)
Average optimal:	= 0.50 (0.2 – 0.8)

Must have “OK” to be acceptable.

Electron Multiplier Set:

Pre-Adjustment Voltage:	= 1500
Low Voltage End:	= 1400
High Voltage End:	= 1500

When the EM voltage > 2000 V, it is time to change the electron multiplier.

Space charge Adjustment:

Target:	>= 20000
Val/Iso Optimal:	= 0.25 (+/- 0.05)

Peak threshold:
Intensity should be > 500 for Ion 131.

10^5 gain setting:
600 – 1500 (Maximum: 3000 V)
Final gain setting should equal to 105.
If not adjust the axial modulation +/-0.5 v and run again.

Appendix VI - Procedure for Running Varian Saturn System

3. SETUP A SAMPLE LIST AND START AN AUTOMATIC RUN IN SATURN

- Go to Acquisition.
- Go to the Edit Automation File on the top tool bar.
- Open a Sample list file at \SaturnWS\Data.
- Set the Sample Type of the first line in the Sample List to Autolink.
  - Under Autolink, set the Command field of the first line to [drive:]\saturnws\ssvauto.exe, or browse to the location of the ssvauto.exe file.
  - Set the Other parameters field of the first line to –i (-i stands for initialization).
- Set the Sample Type for all other sample lines in the Sample list to Autolink.
  - Under Autolink, set the Command field to [drive:]\saturnws\ssvauto.exe, or browse to the location of the ssvauto.exe file;
  - Leave the Other parameters field blank – **make sure there is no** "-i" **in this field**.
- Click on the "Datafile" button on the bottom of the screen, use the default settings, and create a new folder for storing all files in it (i.e.: MAY032001).
- Click the "RecalcList" button, check the "create and update a new recalclist" box.
  - Update the information according to the analysis date.
  - Go to File and save as (i.e.: 050301a.smp), then Exit.
- To start a Sequence, go to Automation.
  - Open [drive:]\SaturnWS\Data\VOC.seq.
  - Update the method file and samplelist file
  - Click on Begin to start the automatic run.

Appendix VI - Procedure for Running Varian Saturn System

4. POST-ANALYSIS PROCEDURE:

- From the Saturn View tab of the Star tool bar, go to Quantitation, then Process/-Review Recalc list.
- Browse and load the Method file (i.e., ReproSat3.mth).
  - ♦ Rename the method according to the analysis date (i.e., Repro071201Sat3.mth).
  - ♦ Go to ACS Ed from the Star Tool Bar, load the above method, make the 5 compounds CH3Br, Isoprene, Freon 113, DCP, and Styrene Inactive.
- Browse and load the Recalc list file (i.e. 071201.rcl).
- Edit the Recalc list as follows:
  - ♦ The first line should be “New Calibration Block”
  - ♦ The next two lines should be the calibration standard, ALM046027, with the Sample Type “Calibration” selected.
    - Note: The standard is repeated twice in order to update the retention times in the method. This is a a glitch in Saturn Software.
  - ♦ Save this modified Recalc list (i.e., 071201cal.rcl).
  - ♦ Click the “Process” button to process the standard file and update the calibration factors and retention times of the method.
- Review the standard data file ALM046027 for compound ID, peak integration, etc. and edit if necessary.
- Edit the method with ACS Ed again.
  - ♦ Make the 5 compounds CH3Br, Isoprene, Freon 113, DCP, and Styrene Active and leave all others inactive.
  - ♦ Generate another recalc list from original list (i.e., 071201.rcl).
  - ♦ Delete everything except the standard ALM029258
  - ♦ Change the Sample Type to Calibration, and repeat the ALM029258 line.
  - ♦ Save this modified Recalc list (i.e., 071201cal1.rc**l**).
  - ♦ Click the “Process” button to process the standard file and update the calibration factors and retention times with the modified method.
- Review and edit the data file ALM029258 for compound ID, peak integration, etc. and edit if necessary.

Appendix VI - Procedure for Running Varian Saturn System

- Edit the method with ACS Ed again, making all the compounds Active.
- Load the original Recalc list file (i.e., 071201.rcl).
- Process all the data files with the updated method.
- Go through each data file, review, re-identify and reintegrate as needed.
- At the calibration standard, print out the full 17 page Sample report so that one Run Log file can be included with all reports.
- Next, generate a peak summary report.
  - Go to System Control tab, then to File\Recalc list, and open the Recalc list file
  - Add a line to the end of the data file list with a Sample Type “Print Summary”.
  - Make sure that the “Enable Automated Printing” is checked on
  - Click the “Begin” button, “OK”, and select the method for the summary repot – SumSat3.mth.
  - Select the “Print” button and click on “OK” to send a brief sample report, a compound report, and the summary report to the printer, and generate a “.csv” file.
- After the csv file is generated, rename it (i.e., SA071201C.csv). This files is used for transferring data to LIMS.

Appendix VI - Procedure for Running Varian Saturn System

5. Turbo Pump Shutdown.

- From System Control, go to the Shutdown screen and click on the Shutdown tab.
- The display for the shutdown program will appear.
- Click on Shutdown.
- The Turbo Pump System shutdown sequence takes at least 30 minutes.
- After the GC and MS temperature zones are reduced to less than 80 ^{o}C, **turn off main power.**
- Then manually vent the system using the lever on the front panel for 1 second and close the lever.
- Wait for 5 minutes and open the vent again for at least 5 more minutes.
- The system will now be ready for service.

6. Turbo Pump Startup.

- From System Control, go to the Shutdown screen.
- While in Shutdown screen, turn on the main power.
- The startup sequence takes at least 30 minutes
- The turbo pump speed should reach to 100% in two minutes.
  - ♦ Click “Reset” if it’s not powering up.

Appendix VII - Procedure for Running Varian/Agilent System

1. AUTOTUNE THE SYSTEM

A) From the GC/MS, Instrument #1, idle.m, do “Perform MS Autotune…”.

B) Select “Autotune”, then “OK”.

C) Review the Autotune report.

2. SETUP THE SAMPLE LISTS AND START AN AUTOMATIC RUN

- Go to Star’s “System Control – Concentrator 1”.
  - In the “Automation File Editor”, go to “Open Sample List”, open a previously used list in the \data directory, update it with new sample information and save (i.e., \data\feb1303.smp).
  - Go to “Open Sequence List” and open \data\voc.seq, update the sequence with the new sample list and then click “Begin” to start the sequence.
- Go to Chemstation’s “GC/MSD – Instrument #1 MSTOP/Enhanced”.
  - Under Sequence “Load…”, find a sequence file under \HPChem\1\Sequence, such as Feb1303.s.
  - Click “Edit Sample Log Table”, update the sample list same as in Star, and add a line at the end, such as “13 sample 1 feb1313 idle ln2”.
  - Go to “Load and Run Sequence…”, select “Full Method”, then “Inject Anyway”, update the sequence name in the sequence comment, select the data file directory, then click “Run Sequence”.

Appendix VII - Procedure for Running Varian/Agilent System

3. PROCEDURE FOR DATA ANALYSIS

- Calibration Method Update
  - ♦ Select the main calibration standard file, go to “Quantitate” and then select Calculate.
  - ♦ Go to “View”, select “QEdit Quant Result”, go through the manual identification and integration process for all target compounds, Exit and Save file.
  - ♦ Go to “Calibrate”, select “Update…/Update one level”, answer “NO” to “Re-quantitate”, select “Recalibrate”, “Replace Response and Retention Time”, then click “Do Update”.
  - ♦ Load another standard sample file that may have a target compound in it, such as Acrolein and repeat QEEdit Quant Result” as above.
  - ♦ Go to “Calibrate”, select “Edit Compounds”, and then go to Page 3 to update the response amount.
  - ♦ Save the method.
- Reprocess Sample Data Files
  - ♦ Useing the updated method, load each data file, go through “QEdit Quant Result” as above, and print the sample report as needed.

4. PROCEDURE FOR CUSTOM REPORT

- From Quantitate, select “Custom Reports…”.
- From Control Panel, select “Create new Database”, the click “OK”.
- Add “Sample Name” to the Header; add “Retention Time”, “Response”, and “Amount” to “All Compounds”, and then click “OK”.
- Name the custom report file (i.e., FEB1303.crd) in the directory of \HPCHEM\Custrpt\MetaFile\.
- **T**he .crd file can be opened and edited in MS Excel.

Appendix VIII: Target Analyte LODs and Highest Calibration Concentration

ALM046027, 10/26/2000

			Multipoint Analysis	
Target Compound	Published LOD (ppb)	Calculated LOD (ppb)	Correlation Coefficient R	Highest Calibrated Concentration (ppb)
MTBE	0.3	0.02	0.9998	23.60

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Appendix IX: Quadrupole and Ion Trap Technology

The following information regarding Quadrupole and Ion Trap technology is quoted from the following source:

> Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Edition, Compendium Method TO-15, “Determination of Volatile Organic Compounds (VOCs) In Air Collected In Specially-Prepared Canisters And Analyzed by Gas Chromatography/Mass Spectrometry (GC/MS)”, EPA/625/R-96/010b, January 1999, pages 15-8, 15-9, and 15-53.

The entire method can be obtained from http://www.epa.gov/ttn/amtic/airtox.html.

“**7.2.2.3.1 Linear Quadrupole Technology**. A simplified diagram of the heart of the quadrupole mass spectrometer is shown in Figure 6. The quadrupole consists of a parallel set of four rod electrodes mounted in a square configuration. The field within the analyzer is created by coupling opposite pairs of rods together and applying radiofrequency (RF) and direct current (DC) potentials between the pairs of rods. Ions created in the ion source from the reaction of column eluates with electrons from the electron source are moved through the parallel array of rods under the influence of the generated field. Ions which are successfully transmitted through the quadrupole are said to possess stable trajectories and are subsequently recorded with the detection system. When the DC potential is zero, a wide band of m/z values is transmitted through the quadrupole. This "RF only" mode is referred to as the "total-ion" mode. In this mode, the quadrupole acts as a strong focusing lens analogous to a high pass filter. The amplitude of the RF determines the low mass cutoff. A mass spectrum is generated by scanning the DC and RF voltages using a fixed DC/RF ratio and a constant drive frequency or by scanning the frequency and holding the DC and RF constant. With the quadrupole system only 0.1 to 0.2 percent of the ions formed in the ion source actually reach the detector.

7.2.2.3.2 Ion Trap Technology. An ion-trap mass spectrometer consists of a chamber formed between two metal surfaces in the shape of a hyperboloid of one sheet (ring electrode) and a hyperboloid of two sheets (the two end-cap electrodes). Ions are created within the chamber by electron impact from an electron beam admitted through a small aperture in one of the end caps. Radio frequency (RF) (and sometimes direct current voltage offsets) are applied between the ring electrode and the two end-cap electrodes establishing a quadrupole electric field. This field is uncoupled in three directions so that ion motion can be considered independently in each direction; the force acting upon an ion increases with the displacement of the ion from the center of the field but the direction of the force depends on the instantaneous voltage applied to the ring electrode. A restoring force along one coordinate (such as the distance, r, from the ion-trap's axis of radial symmetry) will exist concurrently with a repelling force along another coordinate (such as the distance, z, along the ion traps axis), and if the field were static the ions would eventually strike an electrode. However, in an RF field the force along each coordinate alternates direction so that a stable trajectory may be possible in which the

ions do not strike a surface. In practice, ions of appropriate mass-to-charge ratios may be trapped within the device for periods of milliseconds to hours. A diagram of a typical ion trap is illustrated in Figure 7. Analysis of stored ions is performed by increasing the RF voltage, which makes the ions successively unstable. The effect of the RF voltage on the ring electrode is to "squeeze" the ions in the xy plane so that they move along the z axis. Half the ions are lost to the top cap (held at ground potential); the remaining ions exit the lower end cap to be detected by the electron multiplier. As the energy applied to the ring electrode is increased, the ions are collected in order of increasing mass to produce a conventional mass spectrum. With the ion trap, approximately 50 percent of the generated ions are detected. As a result, a significant increase in sensitivity can be achieved when compared to a full scan linear quadrupole system."

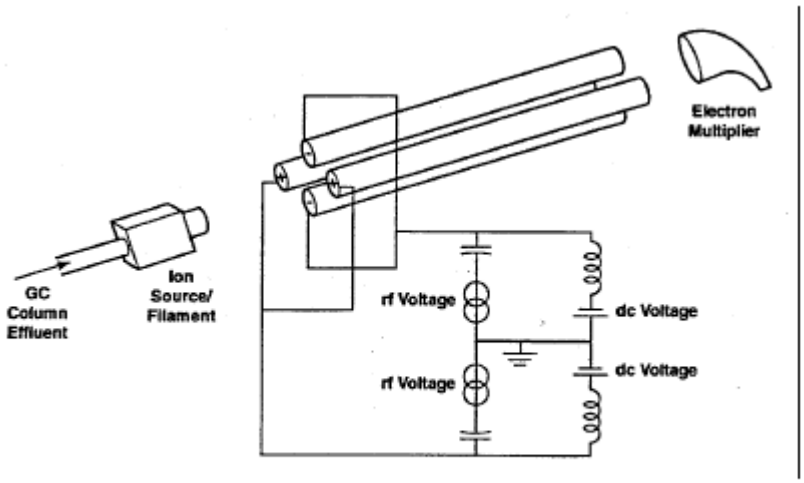

Figure 6. Simplified diagram of a quadrupole mass spectrometer.

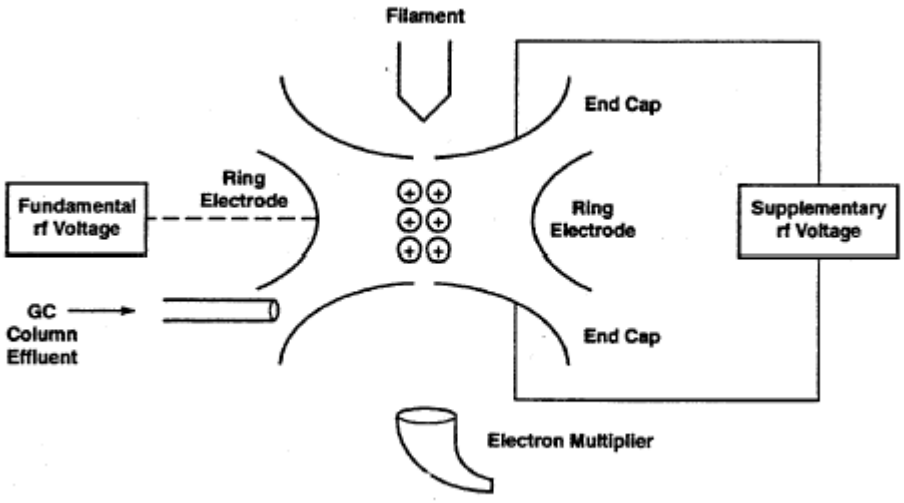

Figure 7. Simplified diagram of an ion trap mass spectrometer.

Appendix X: Note on Agilent and Hewlett-Packard

The Agilent equipment, manuals, and references used in this method may in fact be labeled as Hewlett-Packard. Agilent Technologies was spun off from the Hewlett-Packard Company in 1999. It took with it the portion of the Hewlett-Packard Company that produced analytical equipment. Therefore, Agilent and Hewlett-Packard can be used interchangeably with respect to the analytical equipment referenced in this SOP.

Appendix XI: Revision History

Revision Number	Approval Date	Comments
1.00	July 1, 2002	Initial Draft SOP
2.00	June 15, 2003	This Revision

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